MECHANOCATALYTIC DEPOLYMERIZATION OF LIGNIN

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MECHANOCATALYTIC DEPOLYMERIZATION OF LIGNIN

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SUMMARY

In this work, mechanochemical reactions were performed to depolymerize organosolv lignin with sodium hydroxide in a mixer ball mill at ambient conditions. GPC analysis revealed rapid depolymerization into small oligomers occurred within minutes of milling time, followed by a slower reduction in average relative molecular weight over the next eight hours of milling. Additionally, monomeric products were identified and quantified by GC-MS. The extent of depolymerization appeared to be limited by condensation reactions that form bonds between products. Suppression of these condensation reactions could be achieved through the addition of methanol as a scavenger or adjustment of the moisture content of the feedstock. These modifications resulted in lower average relative molecular weights and higher monomeric yields.

The second portion of this work focuses on the mechanocatalytic depolymerization of lignin under ambient conditions using a variety of solid acid and base catalysts. The use of solid catalysts provides an easier separation from reaction products than sodium hydroxide, which will result in cost savings in industrial applications. Of the catalysts tested, only $Mg(OH)_2$ proved to catalyze significant depolymerization, as determined by a decrease in relative average molecular weight measured by GPC, and creation of substantial yields of monomers as measured by GC-MS. Depolymerization with $Mg(OH)_2$ was not as effective as sodium hydroxide catalyzed depolymerization, with smaller reductions in molecular weight and lower production of monomers for similar milling times. However, $Mg(OH)_2$ was able to be easily completely recovered after the reaction through filtration, which was not possible with sodium hydroxide.

The final section of this work involved the construction of a modified milling reactor to facilitate mechanocatalytic hydrogenation reactions at ambient conditions. Reactions of lignin model compound diphenyl ether using a Pt/Al_2O_3 catalyst revealed conversion to dicyclohexyl ether, cyclohexanol, and cyclohexanone. GC-MS quantification of products showed that reactivity was low for the first hour of milling, followed by a large increase in conversion at two hours of milling. This was followed by a slower increase in conversion between two and eight hours of milling. The volatile products of this reaction were carried out of the reactor by the effluent hydrogen stream and collected in a condenser downstream. The reactor designed for this work can be envisioned to provide an environment in which to simultaneously perform lignin depolymerization and hydrogenation reactions, creating a one-pot system for the creation and separation of fuel precursors.

CHAPTER 1. INTRODUCTION

1.1 Lignocellulosic Biomass and Lignin

Concerns raised over the ultimate depletion of fossil fuel resources has stimulated the search for renewable sources of fuel to serve as a viable replacement for the increasingly industrialized world.[1] The most promising solution to this problem is to develop chemical processes for the efficient conversion of lignocellulosic biomass into liquid fuels, such as ethanol.[2] Lignocellulose refers to portions of plant material that consists of cellulose, hemicellulose, and lignin, and makes up nearly 90% of all plant material on a dry basis.[3] Representations of these three compounds may be seen in Figure 1. Cellulose is the most utilized of the three, due to its abundance in lignocellulose (35-50%) and its regular, repeating structure.[4] Cellulose is comprised of only linked glucose monomer units, making it easier to obtain high selectivities of singular conversion products from it, such as glucose or glucose-derived products. In comparison, hemicellulose contains five types of sugar monomers, and lignin is made from various oxygenated phenyl-propane units.[4] Both hemicellulose and lignin are three dimensional, amorphous, cross-linked polymers with random, non-repeating structures.[4] The proportions in which common monomers are present within these two molecules are often related to the species of plant which served as their source material.[5] These attributes make hemicellulose and lignin more difficult to utilize as feedstocks for fuels and chemicals. Therefore, many industrial processes for converting biomass separate the cellulosic portions from the hemicellulose and lignin.[1, 2, 4] The cellulose is then chemically valorized, while the leftover portions are typically burned as low value fuels for heat energy.[5]

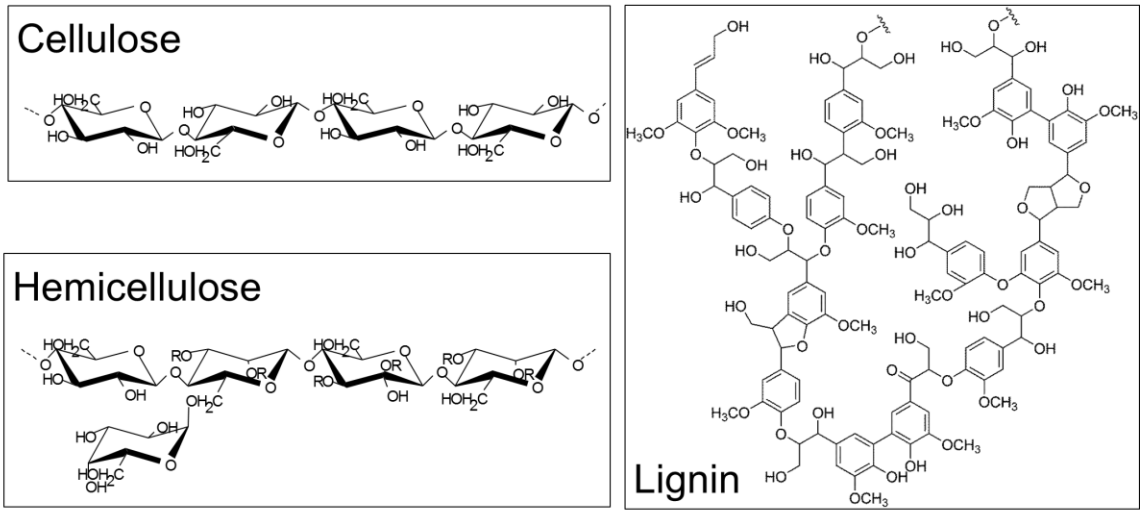

Figure 1: Cellulose is a one-dimensional polymer consisting of glucose units. Hemicellulose contains various sugar monomers in an amorphous, crosslinked structure. Lignin is comprised of primarily functionalized phenyl-propane units in a complex, three-dimensional, amorphous structure. The above representation of lignin is taken from Rak et al.[6]

Lignin can comprise 10-35% by weight and up to 40% by energy content of lignocellulosic biomass. Yet it is often viewed as a waste rather than a potential feedstock for chemical upgrading to biofuels.[5, 7] The molecular structure of lignin is one of the primary reasons for its underutilization in the biofuel industry. The complex three-dimensional amorphous structure gives lignin poor solubility in most conventional solvents.[8] Therefore, harsh conditions (e.g. elevated temperatures, pressures) or expensive unconventional solvents are frequently necessary in order to dissolve lignin for the purposes of performing depolymerization reactions using heterogeneous catalysis.[5] As evidenced by Figure 1, the variety and irregularity of monomeric species in lignin also present an obstacle to valorization, making it difficult to produce specific products with a high yield.[4] Often, difficult separation techniques are required to isolate distinct products.[5] For example, Kang et al. describes a method of using twelve separate extraction

steps to sort 100 lignin derived products of liquefaction into four broad groups of substances.[9] Through this, the authors were only able to successfully recover 28.3 wt % of the original lignin sample.

Despite these challenges, several solutions with varying degrees of success have been suggested.[5] For example, lignin can be converted directly to small molecules through a gasification or pyrolysis pathway.[10] The molecules produced by this method can be converted into chemicals traditionally produced from petroleum. Unfortunately, this process requires large energy consumption, and is not environmentally sustainable for the production of fine chemicals. Another strategy involves depolymerization, defunctionalization, and refining through several catalytic steps.[10] Conversion through this process involves numerous separate reactions, each adding to the total cost of the process. Finally, direct conversion to low yields of valuable chemicals is possible through the use of highly selective catalysts.[10] These catalysts attack only specific portions of the lignin structure, leaving most of the molecule as unreacted or as unwanted byproducts. For all of these methods, single chemicals are not produced in high yields, due to the high degree of heterogeneity of the monomers present in lignin. Thus, separation technologies remain an important and expensive part of the process.[5]

1.2 Mechanocatalysis

Many chemical reactions require an initial or continuous supply of energy to drive their progress. In most instances, this energy is supplied through the addition of heat, in what is known as a thermochemical reaction.[11] However, thermal energy is not the only form of energy that can successfully drive a reaction. In electrochemistry and

photochemistry, the necessary energy is provided by electrons potential or photons.[11] Although far less explored, it has been shown that mechanical energy can also greatly influence the progress or path of a reaction.[12]

Publications dating back to the nineteenth century have shown that halides can be separated purely by compressive mechanical energy supplied by a mortar and pestle.[13] Although researchers since then have developed more effective methods for supplying mechanical energy to a system, such as by milling or ultrasound, much of the work in the field of mechanochemistry has remained primarily focused on inorganic chemistry.[14] Mechanical milling can be used to combine various materials into new homogenous alloys,[15, 16] composites,[17, 18] or oxides,[19-21] frequently with particle sizes on the nanoscale. Particles produced through mechanochemistry may be amorphous, crystalline, and in some cases, even co-crystalline.[14]

Mechanical energy has also been shown to have the potential to alter the structure and properties of catalysts, in addition to the ability to synthesize new catalysts from raw materials.[14, 22-24] Ishida et al. dispersed gold nanoparticles on coordination polymers, carbon, and metal oxides.[25] Another group of researchers produced a composite MgH2-/TiH2 catalyst directly from milling magnesium and titanium powders under high hydrogen pressure.[22] Additionally, there has been extensive evidence that metal organic frameworks (MOFs)[26-30] and zeolite imidazolate frameworks (ZIFs)[14] can be produced in solventless mechanochemical systems.

Extensive evidence of mechanically induced homolytic bond cleavage has been reported for numerous classes of molecules.[31] These homolytic cleavages of covalent

bonds can produce radical molecules in kinetic rates similar to thermally activated processes of comparable energy inputs.[32-34] Mechanically induced heterolytic bond cleavage, conversely, has received less attention and until recently was not considered feasible. However, in 2002, Aktah et al. successfully induced hydrolysis reaction of a poly(ethylene glycol) molecule in an AFM experiment.[35] The success of this experiment has paved the way for an entire new class of chemical reaction pathways to be discovered and studied. Numerous organic reactions have been successfully accomplished under mechanochemical conditions, including Knoevenagel condensation,[36] the Domino oxa-Michael-aldol reaction,[37] the Wittig reaction,[38] direct oxidative amidation,[39] solvent-free peptide synthesis,[40] the Sonogashira reaction,[41] the Suzuki reaction,[42] and the Heck reaction.[43] It is likely that many other reactions will be proven to be feasible in a mechanochemical system.

One of the more interesting advantages offered by mechanochemistry is the possibility of solid-solid interactions. The added energy from impact or friction within a mechanochemical system allow for reactions between solids that would be infeasible for a thermochemical system. The reason for this is often attributed to a hypothesis known as hot spot theory, in which mechanical energy can produce local and nearly instantaneous regions of high temperatures.[14] The 'hot spots' created from impact or friction can reach well above 1000 °C, yet may only last on the order of 10^{-3} to 10^{-4} s.[44] This results in situations where solids may have access to the energy required to interact and react with each other during the short time span of an impact, yet ultimately remain in the solid state after the impact has passed.[45] This allows for reactions between materials that may have

not previously been considered, due to solubility limitations in relation to heterogeneous catalysis applications.

Although mechanochemistry can offer immense cost benefits such as operation without elevated temperatures and pressures or the need for post-process solvent removal by distillation, one must consider the amount of energy required for the process of milling or other mechanical action. If the mechanical energy input exceeds the energy input of more conventional processes, the attractiveness of mechanochemistry is greatly diminished. However, many laboratory scale ball mills have been shown to be relatively energy efficient, consuming on the order of 100-150 W.[46, 47] Additionally, laboratory scale mechanochemical reactions run to completion in significantly reduced time scales compared to thermochemical reactions of similar natures, in many cases below an hour of reaction time.[14] Though there is very little evidence of industrial scale applications of mechanochemistry, preliminary data given seems to indicate that the cost benefits will remain as reactions increase in scale.

1.3 Mechanocatalytic Depolymerization of Biomass

The use of mechanical energy for biomass conversion has long been a popular pretreatment method in the biofuels industry. Pretreatment in a mill can successfully reduce the overall molecular weight of biomolecules, as well as disrupt crystalline regions in the structure.[48] This makes the biomass more susceptible to subsequent hydrolysis or other chemical reactions to convert it into more useful fuel or fine chemical precursors. However, mechanically pretreating biomass with the intent of large scale cleavage of chemical linkages typically requires high energy input and longer milling times.[48] Recently, it has

been discovered that mechanical pretreatment and the subsequent chemical treatment steps can be combined into a single step, commonly referred to as mechanochemistry or mechanocatalysis, greatly increasing the efficiency and effectiveness of both steps.[49] With this method, the energy provided by the mechanical impacts of the milling process provides the necessary energy for the hydrolysis, removing the need for elevated temperatures and pressures. Thus, the mechanocatalytic reaction can be effectively carried out at ambient conditions. Furthermore, the mechanical action of the mill is strong enough to induce chemical reactions in the absence of a solvent, which allows for mechanocatalytic reactions to take place in the solid state.

The application of mechanochemistry to drive a catalytic chemical reaction with biomass was first described in a patent in 2009.[49] This first patent by Blair describes a process for the production of soluble sugars from cellulose through milling in the presence of a solid acid material. The authors note that cellulose can be effectively depolymerized in this manner without the need of a solvent or elevated temperatures or pressures. Various solid acid catalysts were tested, and it was shown that the strength of the acid sites on the catalyst were directly related to its performance. Blair also made the important note that because the presumed reaction mechanism is hydrolysis, the inherent small water content of the cellulosic material and the catalyst play important roles in the progress of the reaction. Through this patent, Blair envisioned a process that allowed for rapid, efficient depolymerization of cellulose followed by a simple isolation of water soluble products and recovery of catalyst.

This work was further expanded by the same authors in a paper in 2010.[50] They investigated several cellulosic feedstocks, solid acid catalysts, and milling types. Through

this, the authors were able to convert 84% of a cellulose sample into water-soluble oligomers after only 3 hours of milling using delaminated kaolinite as a catalyst. Analysis of the monomeric species produced revealed amounts of glucose, fructose, and levoglucosan. After prolonged mechanocatalytic treatment, 5-hdroxymethylfurfural (HMF) was also detected. The authors also found that the specific surface area of the solid acid catalyst was directly related to its ability to produce water soluble oligosaccharides. Generally, layered solid acids were the most effective catalysts because the layered structure breaks down under the mechanical stresses of the milling, leading to a higher specific surface area. Finally, the authors attempted to study the kinetics of the mechanocatalytic hydrolysis reaction. Because the reaction occurs in a solventless system, estimations of reactant and product concentrations were expressed as mass/free volume. With this estimation, the reaction was found to be roughly second order in nature, matching thermochemical hydrolysis reactions of cellulosic material.

Numerous researchers also found that strong acids like HCl or H_2SO_4 offer several advantages as catalysts for mechanochemical conversion of biomass compared to solid acid catalysts.[51-56] Through acid-impregnation pretreatment methods, cellulosic material was shown to be able to fully depolymerize into water-soluble oligosaccharides after only 2 hours of milling.[51] However, despite high conversions into oligomers, production of monosaccharides was relatively low.[53] The reason for this is largely considered to be due to repolymerization by condensation reactions that occur simultaneously with depolymerization reactions.[51, 54, 55, 57] Fortunately, the impregnated acid is retained in the product mixture and can be reused in subsequent downstream processes. Therefore, the water soluble oligosaccharides produced by mechanocatalysis can be easily hydrolyzed

into high yields of monomeric sugars (91% conversion of glucans to glucose, 96% conversion of xylans to xylose) in an aqueous solution with the reused impregnated acid.[51, 58]

The process of mechanocatalysis has also been tested on full lignocellulosic feedstocks, rather than just samples of cellulose.[51] By using a strong acid impregnation pretreatment, lignocellulosic feedstocks can be converted into high yields of water-soluble oligosaccharides through milling, in addition to amounts of lignin oligomer products.[55] When post-treatment saccharification is carried out in an aqueous solution, the oligosaccharides are hydrolyzed into high yields of simple sugars. Conversely, the lignin portions of the original sample undergo condensation reactions during this saccharification step, removing them from solution. This repolymerized lignin residue can be easily filtered out, leaving only the simple sugar solution behind. Through this, a process to efficiently retrieve simple sugars from lignocellulose can be designed.

The application of mechanocatalysis has largely been seen as the first step for conversion of biomass into important platform chemicals. For example, the sugars produced from this method will readily undergo conversion by hydrogenolysis to sugar alcohols to conversions up to 94% yield in the presence of Ru/C at 160 °C.[53] Alternatively, these sugars may be converted to furfurals or HMF in up to 80% yields with the use of $AlCl_3$ catalysts in a biphasic reactor at 170 °C.[52] The addition of n-butanol and heating to 117 °C will facilitate the production of butyl glycosides in yields of up to 62%.[59] Given that the development of mechanocatalysis for biomass conversion is still in relative infancy, it should be expected that many more applications will arise in the future.

In contrast to the interest in valorization of cellulosic material through mechanocatalysis, few attempts have been made to apply the same technology to the depolymerization of lignin. However, the advantages offered by mechanocatalysis seem particularly suited to address the difficulties of converting lignin. The conversion of lignin typically requires expensive solvents and harsh conditions, which has prevented it from becoming more than a waste product.[5, 8] Because mechanocatalytic reactions can operate without a solvent and at ambient temperatures and pressures, they should be an ideal approach for overcoming the traditional issues of lignin depolymerization.

In 2013, Kleine et al. performed a series of mechanocatalytic experiments on lignin and lignin model compounds, using several strong bases as a catalyst.[60] By selecting several model dimers containing a β-O-4 bond that is one of the most common linkages in lignin, the authors identified conditions under which it could be cleaved. Among the catalysts tested, solid sodium hydroxide proved to be the most effective. The authors also investigated organosolv lignin samples under the same mechanocatalytic conditions, and measured changes in the relative abundance of linkages by 2-D HSQC NMR. This showed that sodium hydroxide can effectively cleave β-O-4 linkages not only in model compounds, but also in a larger lignin molecule.

In this thesis, I will further investigate the application of mechanochemistry for lignin depolymerization. The effects of milling organosolv lignin with sodium hydroxide will be shown by analysis of molecular weight, abundance of linkages, and identification of monomeric products. The effects of adding methanol as a scavenger for reactive intermediates in order to suppress unwanted condensation reactions will also be examined. Moreover, the use of solid acid and base catalysts for mechanochemical conversion of

organosolv lignin will be illustrated by molecular weight analysis and identification of monomeric products. Finally, a modified reactor milling vessel will be designed and constructed to perform mechanochemical reactions under a hydrogen atmosphere, in order to perform hydrogenation reactions on lignin model compounds.

CHAPTER 2. MECHANOCHEMICAL DEPOLYMERIZATION OF LIGNIN AND QUENCHING OF REACTIVE INTERMEDIATES

2.1 Introduction

Recently, there has been an increased interest in using lignocellulosic biomass to produce biofuels and other chemicals.[61] The U.S. Department of Agriculture and the Department of Energy have mandated that 20% of liquid transportation fuel and 25% of chemicals and materials should be derived from biomass by 2022, and this has driven research in the conversion of raw biomass into valuable products.[62] While many promising concepts have been developed for the conversion of cellulose and hemicellulose, the lignin fraction of lignocellulosic biomass remains underutilized.[63] In 2004, the pulp and paper industry alone produced 50 million tons of extracted lignin worldwide, and only 2% was for commercial products other than low-value fuel.[5] For lack of better uses, about 25% of the total energy use of paper mills in 2010 was obtained from burning processing byproducts (which include lignin).[64] Therefore, the effective and efficient valorization of lignin has great potential.

Lignin does not have the regular, repeating structure cellulose has, but instead consists of a three-dimensional amorphous polymer comprised of aromatic rings of varying functionalization, primarily hydroxyl, methoxy, and propyl groups.[8] Generally, the three most abundant monomeric species are guaiacyl, syringyl, and p-hydroxyphenyl units.[61]

Due to the presence of different linkages between these monomeric units, lignin is more difficult to depolymerize than cellulose.[65] In addition, lignin exhibits poor solubility in many solvents, which creates difficulty for applications of homogenous or heterogeneous catalytic conversion.[5] Pre-treating lignin with ionic liquids[66] or ozone[67] has been shown to increase the susceptibility of lignin to enzymatic hydrolysis. Steam explosion has also been proven to cleave β-O-4 bonds, which are the most abundant linkages in lignin.[68] Various basic catalysts have been used to depolymerize lignin in batch reactors, and sodium hydroxide has consistently emerged as an effective option.[8, 69] Unfortunately, depolymerization under alkaline conditions generally results in the formation of large amounts of aqueous waste and presents problems for the isolation of products.[5]

Another issue that often reduces the effectiveness of lignin depolymerization is that many lignin fragments can undergo condensation reactions.[5] Repolymerization can occur simultaneously with depolymerization, as reactive intermediates react further to form stable carbon-carbon linkages.[68] Prevention of such condensation reactions has been studied by the usage of scavenging agents, notably phenol or other smaller alcohols like methanol and ethanol.[69-72] These scavengers attach themselves to reactive intermediates before these can interact and cross link with other lignin fragments.

Many processes for the conversion of lignocellulosic biomass require pre-treatment before the depolymerization reaction, which adds an extra step to the process.[5, 8, 48] Milling has been used in academia and industry to reduce the crystallinity of cellulose in biomass. However, this pretreatment often requires long milling times and only leads to a marginal reduction of the molecular weight of components of biomass. As an option for more direct depolymerization of biomass, mechanochemical depolymerization methods have recently

gained considerable attention.[73] Mechanochemistry can use mechanical energy provided by a ball mill to drive a solventless catalytic reaction at ambient conditions. This approach eliminates the issues caused by the poor solubility of biomass polymers (i.e. cellulose, lignin) in most common solvents. Mechanochemical ball milling has been used to produce water-soluble oligosaccharides from cellulose by hydrolysis with both solid acid catalysts and after impregnation with liquid acids[50-53, 56, 57, 74, 75] and to cleave β-O-4 bonds in lignin and model compounds with sodium hydroxide catalysts.[60] Various hypotheses for the way in which mechanochemistry operates have been proposed, including that friction provides energy in the form of high temperature pockets that enable molecules to overcome a solid-solid diffusion barrier,[50, 60] or that mechanical impact deforms molecules resulting in higher, more reactive energy states.[76] Unfortunately, little evidence has been provided in for any of these suggestions.

In mechanochemical experiments with cellulose feedstocks, it has been noted that the production of oligomers in high yields is quite easy, but yields of monomeric products are relatively low.[51] Several theories for this phenomenon have been put forth.[51, 57] Some attention has been paid to the moisture content of feedstock, because the dominant reaction is presumed to be hydrolysis.[50, 51] While the addition of certain quantities of water is necessary to provide an otherwise limiting reactant,[77]addition of excess water can result in a plasticizing effect, which dissipates the mechanical energy from grinding, preventing chemical reactions.[78] Large amounts of water can even make the substrate so sticky that grinding is halted altogether. Another theory for the limited depolymerization is the occurrence of repolymerization reactions,[51, 57] similar to the reactions of intermediates in

thermochemical processes.[51, 54] However, methods for preventing condensation of reactive intermediates in a mechanochemical system have yet to be explored.

In this work, mechanochemical reactions for lignin depolymerization with sodium hydroxide are investigated. Prevention of repolymerization reactions through the use of methanol as a scavenger is also studied. Finally, the effects of the moisture content of the lignin feedstock are explored. Molecular weight analysis of the products is performed by GPC, monomeric products are identified and quantified by GC-MS analysis, and an analysis of chain length distributions is obtained by LC-MS. In addition, linkage motifs of selected samples are examined by HSQC NMR.

2.2 Experimental Section

2.2.1 Materials

Organosolv lignin from beech was obtained from Fraunhofer Institut in Leuna, Germany. Sodium hydroxide (ACS reagent, ≥97.0%, pellets), methanol (ACS spectrophotometric grade, ≥99.9%), methanol (CHROMASOLV® for HPLC, ≥99.9%), tetrahydrofuran (ACS reagent, >99.0%), acetic acid (glacial, ACS reagent, ≥99.7%), and 3,5 dimethoxyphenol (99%) were purchased from Sigma-Aldrich. Hydrochloric acid (ACS reagent, 36.5-38.0%, liquid) and o-xylene (99%) were obtained from Alfa Aesar. Ethyl acetate (ACS reagent, 99.9%) was purchased from Fisher Scientific. d6-DMSO was obtained from Cambridge Isotope Laboratories.

2.2.2 Moisture Content of Organosolv Lignin Sample

Five samples of the original organosolv lignin (2.00 g) were placed in an oven at 105 °C to evaporate the water content of the sample. The samples were weighed periodically to track changes in mass. After 48 hours, when the samples had reached constant masses, the moisture content was calculated as the average of the five samples using the following equation:

$$Moisture\ Content\ (wt\%) = \frac{m_{total\ sample} - m_{dried\ sample}}{m_{total\ sample}} * 100\% \qquad (1)$$

2.2.3 Mechanochemical Reactions

Ball-milling of lignin was performed in stainless steel vessels (25 mL) using a Retsch MM400 ball mill at room temperature. The vessels were equipped with three milling balls each (12 mm diameter, stainless steel). The ball-milling was carried out at 800 rpm (13.3 Hz) for 0 to 8 h. To avoid overheating at long milling times, the mill was stopped for 10 minutes after every 30 minutes of milling. For all tests, the milling vessel was filled with organosolv lignin (1.50 g) and sodium hydroxide pellets (1.50 g). For ion scavenging tests, methanol (0.40 mL) was added to the lignin/sodium hydroxide mixture in the milling vessel. To investigate the influence of the moisture content, water was added to the milling vessel to increase the total moisture content in the sample from its original value of 3.7 wt% to the desired moisture content.

2.2.4 Gas Chromatography – Mass Spectrometry (GC-MS)

The milled samples were dissolved in methanol and diluted to a concentration of 10 mg/mL. The samples were neutralized by addition of hydrochloric acid in an amount equivalent to the sodium hydroxide in the reaction mixture. 3,5-Dimethoxyphenol was used as an internal standard. Samples were filtered using 0.2 μm polypropylene membranes. GC-MS analysis was performed using a Varian (Agilent) 450-GC with a FactorFour™ VF-35ms capillary column (30m x 0.25mm x 0.25μm) coupled with a 300-MS Varian (Bruker) mass spectrometer (EI, 200 °C). The carrier gas was helium at 1.0 mL/min with an autosampler injection volume of 1.0 μL. The temperature of the column was initially held at 70.0 °C for 1.50 minutes, then raised at a rate of 35.0 °C/min to 100.0 °C. The temperature of the column was then raised at a rate of 10 °C/min to 300.0 °C, where it was held for 12.0 min.

Yield of total detected monomeric species was calculated as follows:

$$yield\ (wt\%) = \frac{m_{volatile\ monomers}}{m_{total\ reacted\ sample}} * 100\% \quad (2)$$

It is important to note that GC-MS is not strictly quantitative, and the detector in an MS responds differently for each individual compound measured by the instrument. Fortunately, most of the detected products were substituted aromatic compounds with similar overall molecular structures. These compounds generate similar fragmentation patterns within the MS and thus differences in the response factor between them could be assumed to be minimal enough to obtain rough quantification estimates. For the same

reason, an internal standard was chosen that is an isomer of one of the most prominent products analyzed in order to reduce discrepancies in response factor.

2.2.5 Gel Permeation Chromatography (GPC)

The milled samples were dissolved in THF and diluted to a concentration of 4 mg/mL. The samples were neutralized by addition of hydrochloric acid in an amount equivalent to the sodium hydroxide in the reaction mixture. Samples were filtered using 0.2 μm nylon membranes. An amount of 1.0 μL of each sample was injected into an Agilent PL-GPC-50 with a Refractive Index Detector. THF was used as an eluent with a flow rate of 1.0 mL/min, and polystyrene standards were used for calibration. The data was analyzed using Cirrus GPC software (Version 3).

2.2.6 Liquid Chromatography – Mass Spectrometry (LC-MS)

LC-MS analysis was performed using a modified procedure based on the work of Haupert et al.[79] The milled samples were dissolved in a 50:50 (v:v) methanol/water solution and diluted to a concentration of 100 μg/mL. o-Xylene was used as an internal standard. Samples were filtered using 0.2 μm polypropylene membranes. LC-MS analysis was performed on a Shimadzu LCMS-8060 using an ESI source in negative ion mode with a spray voltage of 5.0 kV. The nebulizing gas flow of nitrogen was set at 3.0 L/min, and the drying gas flow of nitrogen was set at 15.0 L/min. An autosampler was used to inject 6 μL of each sample onto a Phenonenex Luna 5μ Silica column with dimensions 150 mm X 4.60 mm X 5 μm. The mobile phase was a 50:50 (v:v) solution of methanol and water at 0.300 mL/min.

2.2.7 NMR spectroscopy

Milled samples were dissolved in water and diluted to 50 mg/mL. Samples were neutralized by addition of hydrochloric acid in an amount equivalent to the sodium hydroxide in the reaction mixture. Reaction products were extracted into an organic layer of ethyl acetate, and the solvent was subsequently removed under vacuum in a round-bottom flask.

Lignin samples (ca. 50 mg) were dissolved in 600 μL d6-DMSO and transferred to 5 mM Wilmad 535-PP NMR tubes. The solvent contained 0.05% (v/v) tetramethyl silane (TMS) for chemical shift referencing. One-dimensional 1H and two-dimensional 1H-13C heteronuclear single quantum coherence (HSQC) spectra were acquired as described previously[80] at 298 K on a 500 MHz Varian Inova equipped with a Nalorac HCNP triple resonance z-axis pulsed-field gradient probe. Using the BioPack gChsqc pulse sequence, separate HSQC spectra were collected for the aliphatic and aromatic regions of the 13C chemical shift range. Delay times tCH and lambda for 1/4*JCH, were 1.8 ms and 1.6 ms for aliphatic spectra, and 1.45 ms and 1.3 ms for aromatic spectra. The 1H spectral width was 17 ppm and 13C spectral width was 100 or 60 ppm for the aliphatic or aromatic regions, respectively. Spectra were collected with 1024 points (Varian parameter np) and 61 ms acquisition time in the 1H dimension and with 128 transients and 192 or 128 complex points (Varian parameter ni in States-TPPI mode) in the indirect 13C dimension, for aliphatic and aromatic spectra, respectively. Adiabatic WURST decoupling was applied during acquisition. Data were processed using MestReNova 9.01 with 2X zero filling in both dimensions and matched Gaussian apodization in both dimensions. Integration of peak areas used identical elliptical boundaries for all spectra.

2.3 Results

2.3.1 Characterization of Organosolv Lignin Sample

The moisture content of the unmodified organosolv lignin sample was 3.7 wt%. Gel Permeation Chromatography (GPC) analysis showed that the average relative molecular weight was approximately 800 g/mol, which corresponds to between 5 and 6 monomeric units. NMR spectroscopy was used to characterize the unmilled lignin feedstock (Figure 2a). Using volume integrals of characteristic HSQC cross peaks for α, β, and γ protons in the propyl groups of monolignol residues in lignin,[81-84] the relative abundance of the major linkages in the unmilled lignin were estimated to be 57:19:24 for β-O-4 (β-aryl ether), β-5 (phenylcoumaran), and β-β (resinol), respectively. The β-O-4 species comprised several distinct species including a small proportion of linkages to α-oxidized (carbonyl) units. The aromatic region of the HSQC spectrum was used to determine that the ratio of guaiacyl to syringyl units (G:S ratio) was 40:60, which is typical of hardwood lignins.

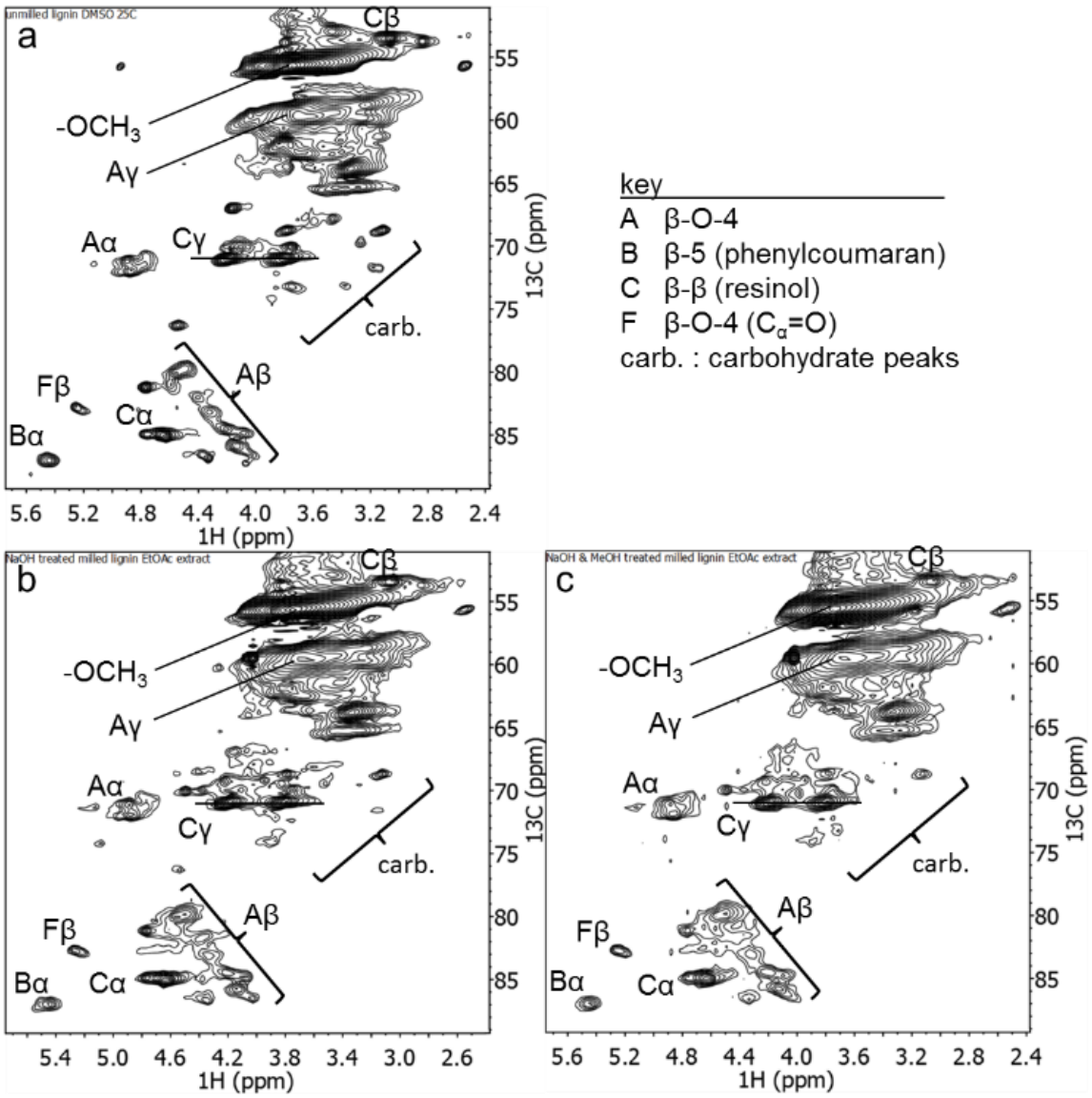

Figure 2: Downfield region of the aliphatic 1H-13C HSQC spectrum showing cross peaks characteristic of different types of linked monolignol building blocks in unmilled lignin in DMSO (panel a), and dried ethyl acetate extracts of mechanocatalytically processed lignin with (panel b) and without (panel c) methanol treatment, in DMSO. Key cross peaks used to determine relative linkage composition between the samples are indicated.

2.3.2 Reactivity studies

The mechanochemical conversion of organosolv lignin with NaOH was performed with pure lignin and after addition of methanol or water. The following sections describe

the analysis of the average relative molecular weight (GPC), nature and approximate yield of monomeric species (GC-MS), distribution of chain lengths (LC-MS), and distribution of linkages (HSQC NMR spectroscopy), before the reactions during the process are discussed.

For studies in which additional water was supplied to the milling vessel, attention was paid to the consistency of the resulting mixture because water has a known plasticizing effect on biomass, which impedes its ability to be ground in a mill.[78] For moisture contents up to 14 wt% the samples remained as powders, but when the moisture content was increased to 20 wt%, the sample possessed physical properties similar to a sludge, and the milling balls stuck to the sides of the container and to each other.

2.3.3 Gel Permeation Chromatography (GPC)

Figure 3 displays the number average molecular weight (M_n), relative to narrow standard calibration with polystyrene standards, as a function of milling time. The lignin sample milled without the addition of any catalysts or reactants underwent only minimal change for the duration of the milling times tested. When sodium hydroxide was added to the milling vessel, the relative molecular weight was reduced from approximately 800 g/mol to 410 g/mol after 8 hours. The majority of this depolymerization occurred within the first 30 minutes of milling, in which the relative molecular weight was around 470 g/mol. The relative molecular weight was slowly reduced to 410 g/mol after 5 hours of milling, and remained at this value up to 8 hours. Inclusion of methanol as an additional reactant in the milling vessel enhanced depolymerization. The initial reduction in relative molecular weight was more rapid, and a value of 400 g/mol was reached in only 5 minutes

of milling. Afterwards, the decrease in relative molecular weight was much slower, but it continued to a final value of under 250 g/mol after 8 hours of milling.

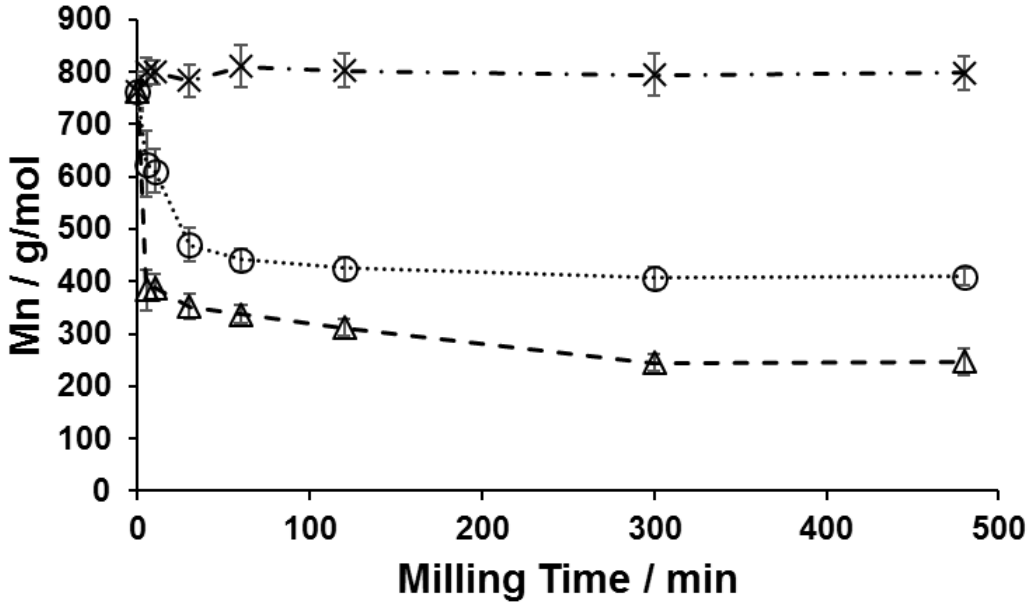

Figure 3: Number average molecular weight (M_n), as determined by GPC, plotted as a function of milling time. Mixtures of 3.00 g uncatalyzed lignin (x), 1.50 g lignin combined with 1.50 g NaOH (○) and 1.50 g lignin combined with 1.50 g NaOH and 0.4 mL of methanol (△) were milled in a mixer ball mill at 800 rpm.

GPC analysis was also performed for samples milled for 2 hours with sodium hydroxide and different moisture content (Figure 4). The moisture contents ranged from that of untreated lignin (3.7 wt%) to 20 wt%. The relative molecular weight of these samples showed a steady decrease up to 18% moisture, where the M_n reached a minimum of 340 g/mol. However, in the presence of 20 wt% moisture, the samples only reached a relative molecular weight of 460 g/mol, larger than the 430 g/mol reached by the unmodified lignin samples with 3.7% moisture.

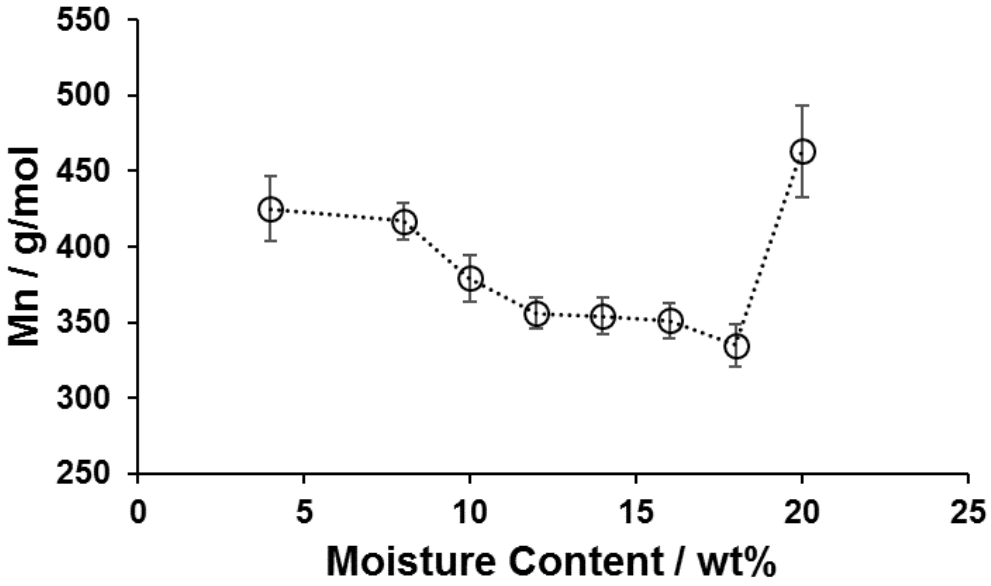

Figure 4: Number average molecular weight (M_n), as determined by GPC, plotted as a function of moisture content of the milled sample. Lignin samples were milled with sodium hydroxide (50:50, w:w) in a 25 mL mixer ball mill for 2 hours at 800 rpm. Each test sample contained 3.00 g of total substrate before addition of water to achieve the necessary moisture content.

2.3.4 Gas Chromatography – Mass Spectrometry (GC-MS)

The products created from the mechanochemical reactions between lignin and sodium hydroxide from 0 to 8 hours were studied using GC-MS. While this technique is not strictly quantitative, it allows for an estimating of the abundance of different products, in particular if they have similar molecular structures. Table 1 shows the monomeric species identified in the product mixture obtained from the mechanochemical reactions. The most abundant of these compounds included phenol, syringol, and guaiacol, which are among the most common monomeric building blocks found in most types of lignin feedstocks. The other monomers present are comprised primarily of similarly functionalized aromatic rings containing hydroxyl, methoxy, and other groups common to

the structure of lignin. Figure 5 shows the combined apparent yield of these monomeric species as a function of milling time.

Table 1: Average apparent selectivity of monomeric species produced by the mechanochemical reaction between lignin and sodium hydroxide after 5 hours.

Compound	Average Selectivity / wt%
Propane, 1,1,3,3-tetramethoxy-	2.35
Phenol	29.42
Guaiacol	7.91
4-methoxy-3-methylphenol	0.39
Creosol	0.34
Phenol, 4-methoxy-3-methyl-	0.25
2,6-dimethylanisole	0.04
4-ethylguaiacol	0.05
4-vinylguaiacol	1.88
o-Eugenol	0.12
Syringol	17.85
Isoeugenol	0.31
Methyl dodecanoate	0.86
2,6-di-tert-butylphenol	0.16
1,2,4-trimethoxybenzene	1.70
3,4,5-trimethoxytoluene	1.16
Canolol (2,6-dimethoxy-4-vinylphenol)	4.10
1,2-dimethoxy-4-(2-methoxyethenyl)benzene	1.12
2,4,5-trimethoxybenzaldehyde	18.85
2,6-dimethoxy-4-(2-propenyl)phenol	5.02
Methyl palmitate	4.12
Octadecanoic acid, methyl ester	2.01

For all of the samples tested, yield of monomeric species increased sharply after only 5 minutes of milling. However, when the milling time was increased to 10 minutes, the yield dropped significantly. As milling time was increased beyond 10 minutes, the yield increased again, reaching a maximum for all samples at 5 hours of milling. By 8 hours of milling, the yield began to decrease once more. The maxima at 5 minutes of milling corresponded to yields of 23% and 20% for samples milled with only sodium hydroxide and samples milled with both sodium hydroxide and methanol, respectively. The maxima at 5 hours of milling produced yields of 25% and 44%. Figure 6 shows yields as a function of increasing moisture content. Monomer yield increased only slightly up to 12% moisture, but a significant maximum of 53% was seen with a moisture content of 14 wt%. When the moisture content was higher than 14 wt%, the yield decreased to a value similar to those seen before the maximum.

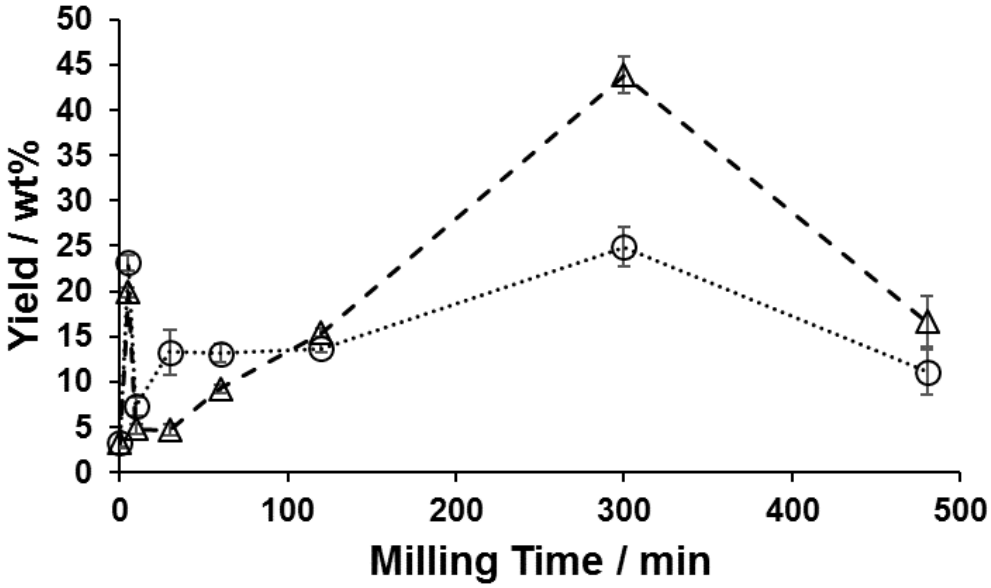

Figure 5: Yield of monomeric species produced, as determined by GC-MS, plotted as a function of milling time. For these experiments, 1.50 g lignin combined with 1.50 g

NaOH (○) and 1.50 g lignin combined with 1.50 g NaOH and 0.4 mL of methanol (△) were milled in a mixer ball mill at 800 rpm.

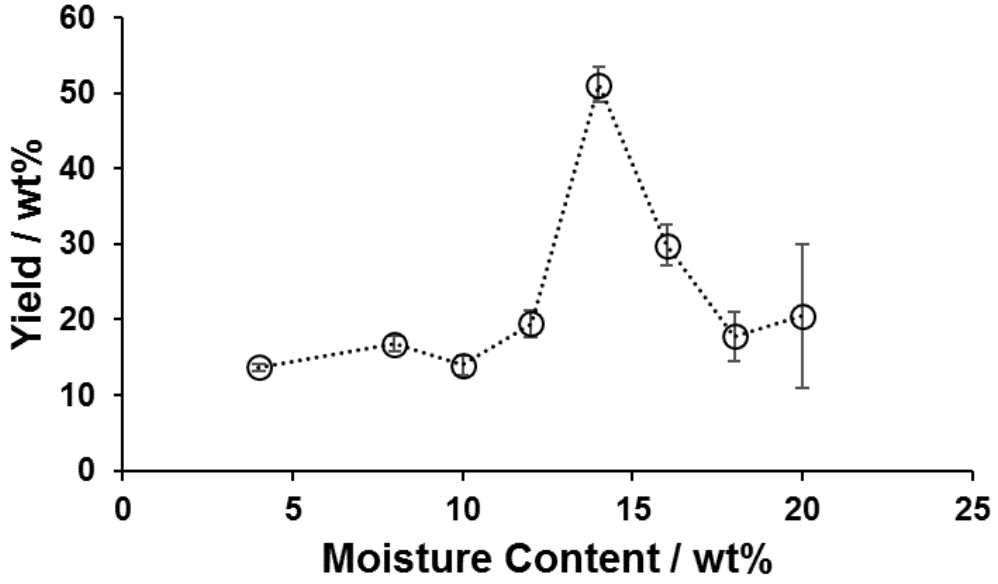

Figure 6: Yield of monomeric species produced, as determined by GC-MS, plotted as a function of moisture content of the milled sample. Lignin samples were milled with sodium hydroxide (50:50, w:w) in a 25 mL mixer ball mill for 2 hours at 800 rpm. Each test sample contained 3.00 g of total substrate before addition of water to achieve the necessary moisture content.

2.3.5 Liquid Chromatography – Mass Spectrometry (LC-MS)

LC-MS analysis was performed to determine the distribution of the products of the mechanochemical reactions based on the size of the various species present. By taking the average monomer molecular weight to be 166 g/mol (based on an average molecular formula of $C_9H_{10}O_3$ from the monomers detected by GC-MS), products were classified as monomers, dimers, and oligomers with chain lengths of 3 or more units, and displayed in Figure 7 as their fraction of the weight of the analyzed sample.

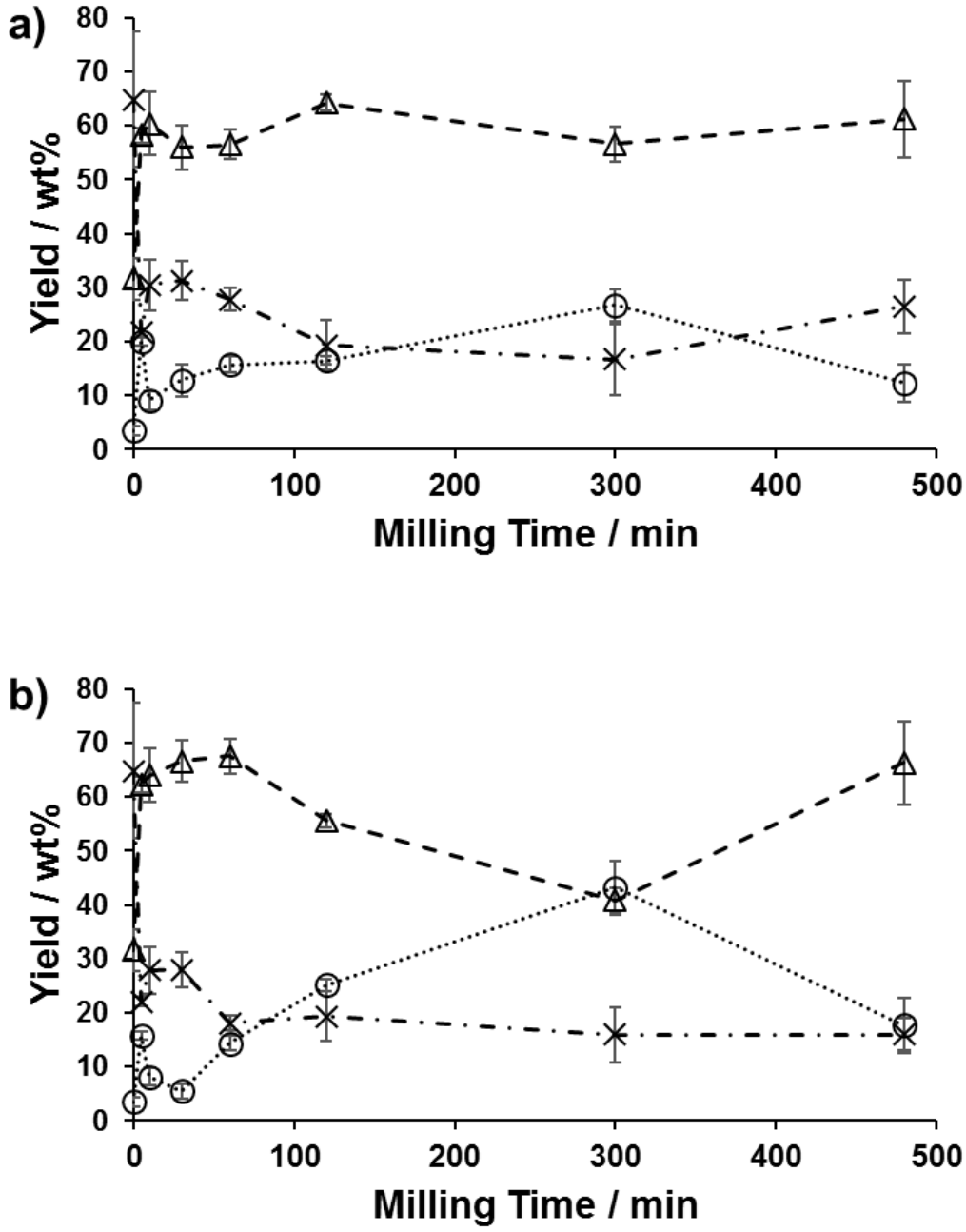

Figure 7: Yield of monomers (○), dimers (△), and trimers and larger oligomers (X), as determined by LC-MS, plotted as a function of milling time. a) 1.50 g lignin combined with 1.50 g NaOH and b) 1.50 g lignin combined with 1.50 g NaOH and 0.4 mL of methanol were milled in a mixer ball mill at 800 rpm.

The monomer yield followed the same trend as the GC-MS results. Examination of the unmilled lignin sample revealed values of approximately 3 wt% monomers, 32 wt%

dimers, and 65 wt% trimers and larger oligomers. Analysis of samples milled with sodium hydroxide (Figure 7.a) and samples milled with both sodium hydroxide and methanol (Figure 7.b) showed that the fraction of oligomers with a chain length of 3 or more dropped to slightly over 20 wt% within only five minutes of milling. This value increased to 30 wt% after ten minutes of milling, before it reached a maximum after thirty minutes and subsequently decreased. For both of these experiments, the majority (between 50 wt% and 70 wt%) of the sample was comprised of dimers after only five minutes of milling and remained the majority for the duration of the milling times tested. The one exception to this was the lignin sample milled with both sodium hydroxide and methanol for five hours, which resulted in the monomer yield slightly surpassing the dimer yield, which dropped to 41 wt%.

As seen in Figure 8, modification of the moisture content between the original 3.7 wt% and 12 wt% produced only slight variation in the distribution of the products formed. With 14 wt% moisture, however, a large amount of monomeric species was produced and the dimer yield dropped significantly. At moisture contents higher than 14 wt%, the monomeric and dimeric yields decreased and increased again, respectively.

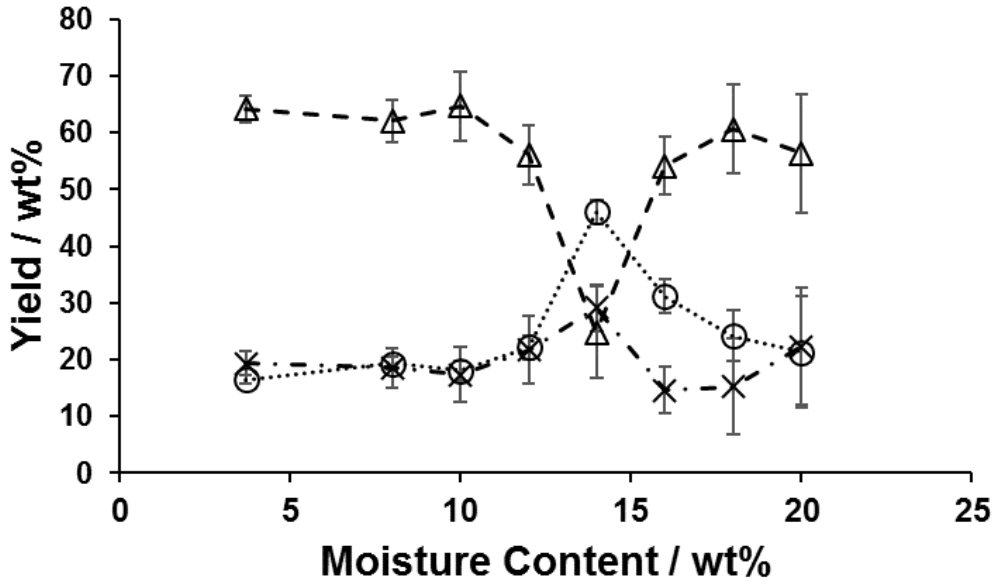

Figure 8: Yield of monomers (○), dimers (△), and trimers and larger oligomers (X), as determined by LC-MS, plotted as a function of moisture content of the sample. Lignin samples were milled with sodium hydroxide (50:50, w:w) in a 25 mL mixer ball mill for 2 hours at 800 rpm. Each test sample contained 3.00 g of total substrate before addition of water to achieve the necessary moisture content.

2.3.6 Heteronuclear Single Quantum Coherence (HSQC) NMR Spectroscopy

Samples milled for 2 hours with NaOH in the presence and absence of methanol were analyzed by HSQC NMR spectroscopy. Compared with the unmilled sample (Figure 2.a), milling with sodium hydroxide changed the relative abundances of β-O-4 (β-aryl ether), β-5 (phenylcoumaran), and β-β (resinol) linkages changed from 57% to 56%, 19% to 16%, and 24% to 28%, respectively (Figure 2.b). Increased peak dispersion in regions containing cross peaks associated with these linkages can be seen as well, most notably for the Aβ and Cγ peaks in panels b and c of Figure 2, suggesting changes that increase structural heterogeneity of the lignin have occurred. If one assumed that the number of β-β linkages is constant because of the resistance of carbon-carbon bonds to cleavage with basic

catalysts,[5] the relative abundance of β-O-4 linkages would to decrease by about 15% during this process. The presence of methanol in the mechanochemical reaction mixture (Figure 2.c) changed the relative proportions of the major linkages towards fewer β-O-4 linkages (45:21:32), corresponding to a 65% decrease relative to a constant number of β-β linkages.

2.4 Discussion

2.4.1 Depolymerization with Sodium Hydroxide

Base-catalyzed depolymerization of lignin in the aqueous phase is a common method for producing simple aromatic monomers. Basic catalysts attack ether bonds, which are both the most abundant[8] and the weakest linkages between the monomeric building blocks.[85] Of these ether linkages, the β-O-4 bond is the most common in lignin, comprising between 45% and 65% of all linkages between monomeric units in various lignin sources.[86] Strong bases like sodium hydroxide are particularly effective at hydrolytically cleaving this bond under various aggressive conditions.[69, 87, 88] On the other hand, non-ether linkages, such as β-5 or 5-5 bonds, are typically resistant to base catalyzed depolymerization[5]. These carbon-carbon bonds can make up as much as one third of the linkages between monomers in lignin.[8]

Kleine et al. showed that the linkages in organosolv lignin and lignin model compounds can be cleaved in base-catalyzed mechanochemical reactions.[60] In this environment, the same ether linkages are cleaved as in typical catalytic processes in the aqueous phase. Milling of lignin model dimers containing the β-O-4 bond in the presence of a strong base, such as NaOH, KOH, or LiOH, resulted in high yields of monomers in

relatively short times. Milling of organosolv lignin and beech wood with sodium hydroxide led to effective cleavage of the β-O-4 linkages. However, only a single time point of 12 hours was provided for the analysis of organosolv lignin depolymerization, which prevents an interpretation of the dynamic effects of mechanochemistry, in particular the simultaneous occurrence of depolymerization and condensation reactions.[60] Furthermore, a milling time of 12 h is too long for a commercially viable process. Additionally, changes in the average relative molecular weight of organosolv lignin and the nature and yield of different products were not reported.

As evidenced by the experiments in the present work, sodium hydroxide is capable of depolymerizing organosolv lignin under mechanochemical conditions. The average relative molecular weight of the sample can be reduced significantly within the first 30 minutes of milling, after which depolymerization slows, and Mn eventually reaches a minimum value. This lower limit rests at approximately 410 g/mol, roughly half of the original average relative molecular weight of the unmilled sample. LC-MS analysis shows that the majority of the resulting product consists of dimers after only 5 minutes of milling. The resistance of the samples to fully depolymerize is indicative of the presence of C-C linkages that are resistant to cleavage using basic catalysts.[8] These stronger carbon-carbon bonds in lignin can be effectively broken in thermochemical cracking reactions, which typically utilize strong Brønsted acid catalysts, such as zeolites.[8] Additionally, the yield of monomers fluctuates between minima and maxima, corresponding to maxima and minima in the yield of trimers and larger oligomers, respectively. This suggests that condensation reactions are taking place simultaneously with the depolymerization reaction, presenting another obstacle to complete depolymerization.

After an initial maximum in the yield of monomeric species after 5 minutes of milling, this value drops sharply. The rapid initial production of monomers in this initial 5 minutes is likely a result of easily accessible regions in the original lignin structure along with weakly bound water molecules. The rapid depletion of the original loosely bound water favors condensation reactions after five minutes of milling, which consumes a portion of the previously produced monomeric species. However, as milling progresses from 10 minutes to 5 hours, more bound water becomes accessible within the structure of lignin,[89] leading to a rise in production of monomers. In this period, condensation reactions can also occur due to localized depletions of water molecules, reproducing β-O-4 bonds or forming new C-C bonds, which are unbreakable by base-catalyzed hydrolysis.[8] Strong evidence for the formation of new β-O-4 bonds is the limited reduction in β-O-4 bonds after 2 hours of milling as observed by NMR, while GPC showed a decrease of M_n to nearly half of its original value. However, the continuous release of bound water ultimately pushes the reaction towards hydrolysis rather than the condensation pathway. Between 5 and 8 hours of milling, the yield of monomers decreases. This is likely related to depletion of bound water released by mechanical grinding, and the decreasing availability of accessible β-O-4 bonds that can be hydrolyzed. An increasing fraction of the remaining linkages appears to be C-C bonds due to their resilience and the formation of additional ones in condensation reactions. Thus, the previously produced monomers are again consumed in the formation of condensation products. This is marked by an increase in the yield of trimers and larger oligomers at 8 hours of milling.

2.4.2 Use of Methanol as a Scavenger for Reactive Intermediates

One of the biggest issues for effective depolymerization of lignin is the prevention of condensation reactions.[5, 8, 90] In base-catalyzed hydrolysis of lignin, unstable intermediates may react with each other to recombine into larger oligomers rather than completing the transformation to stable monomers.[90] The char that is formed in these repolymerization reactions typically contains carbon-carbon bonds that are resistant to cleavage with basic catalysts.[8] A promising approach to prevent condensation reactions from occurring is the addition of scavenging agents that quench reactive intermediates.[69-72] Proton-donating scavengers include formic acid, phenol, 2-naphthol, and various alcohols. The donation of H+ ions to reactive carbanion intermediates has been shown to have a positive impact on reduction of formation of chars through repolymerization reactions in thermochemical reactions.[5] It is important to note that biomass has also been shown to undergo limited depolymerization during mechanical treatment through the formation of radicals by cleavage of ether bonds.[91] However, the production of these radicals in lignin is very slow. One study reported no depolymerization of lignin after 1 week of continuous milling and an eventual yield of only approximately 20 wt% monomers after 4 to 6 weeks of continuous milling.[92] Additionally, the dominant mechanism of cellulose depolymerization in an acid-impregnated, ball-milled mechanochemical system has proven to be through hydrolysis and not the generation of radicals that are known to appear in mechanical pretreatments of biomass.[56] Thus, condensation reactions likely occur due to the generation of ionic species from hydrolysis, not from the formation of radicals.

Repolymerization reactions were shown to reduce the yield of monosaccharides during mechanochemical depolymerization of cellulose.[51, 57] However, viable strategies for the prevention of these condensation reactions have yet to be developed. This may be because the necessity for preventing these reactions is limited due to the sufficient solubility of repolymerized oligosaccharides produced from these reactions in water that allows for simple separation of products and subsequent post-processing steps into monosaccharides.[59, 74, 93, 94] Depolymerization of lignin via mechanochemistry presents a greater challenge due to the lower solubility of lignin oligomers in most solvents compared to oligosaccharides.[64] This presents a significant challenge for product separation and subsequent downstream processing. Thus, the need for prevention of condensation reactions in mechanochemistry of lignin is essential.

To address the issue, methanol was used as a scavenger in the present study, and positive effects on both relative molecular weight reduction and yield of monomeric products were observed. Initial depolymerization was more rapid, and the final average relative molecular weight of the reaction products decreased by an additional 40% compared to the samples milled with sodium hydroxide in the absence of methanol. Furthermore, the maximum monomer yield after 5 hours of milling increased by 75%, and the amount of cleaved β-O-4 bonds detected by NMR after 2 hours of milling increased from 15% to 65%. These results suggest a reduction of the extent to which condensation reactions take place when methanol is added to the reaction mixture. Interestingly, neither the species of monomers detected by GC-MS nor their respective selectivities (Table 1) were altered significantly when methanol was added to the milling vessel. This indicates that in this case, the methanol is donating a proton to reactive carbanion intermediates that

are formed in the reaction, rather than a methoxy ion to a carbocation species. This donated proton can be replenished by the small amount of water in the system, consuming the water and completing the base-catalyzed hydrolysis reaction. However, based on an estimation of an average monomer molecular weight of 166 g/mol the moisture content of the untreated organosolv lignin sample (i.e., 3.7 wt%) is only sufficient for a monomer yield of 35%. Therefore, the observed monomer yield of 44% after 5 hours of milling suggests that a part of the lignin undergoes a solvolysis reaction when methanol is present in addition to the hydrolysis reaction. This solvolysis reaction can continue until the methanol or NaOH are completely consumed, producing sodium methoxide from the sodium hydroxide originally in the system. Base catalyzed solvolysis of ether linkages in lignin using small alcohols using thermochemical methods has been documented in several publications and is mechanistically similar to hydrolysis of ethers and esters, producing basic alkoxides from hydroxides.[88, 95] The methanol can be subsequently regenerated upon the addition of water.[96] The added methanol in the system provides more than enough reactant to achieve the observed 44% yield of monomers. Additionally, solvolysis with methanol has been shown to be less kinetically limited than hydrolysis, which can reduce the chance of intermediates undergoing condensation reactions.[95]

2.4.3 Adjustment of Moisture Content

Base-catalyzed depolymerization of lignin is a hydrolysis reaction.[8] Thus, the amount of water present in the system plays an important role. Generally, water in mechanochemical reactions is provided through the moisture content of the supplied biomass feedstock.[50] Several researchers have suggested that the addition of more water to the system may be needed to achieve the desired reactivity for the depolymerization

reactions.[50, 51] However, the only reported use of increased moisture in a mechanochemical system resulted in a decrease in depolymerization of cellulose.[51] This is because excess water tends to cause plasticization due to the formation of hydrogen-bonded liquid bridges between molecules, leading to a significant reduction of the glass transition temperature.[97] These phenomena prevent efficient mixing and grinding. In the present work, well-controlled amounts of water were added to the lignin to avoid the detrimental plasticizing effects of excess water.

The fresh lignin feedstock contained 3.7 wt% water. Because the hydrolysis reaction requires one water molecule for each linkage broken, the original moisture content is not large enough to allow for hydrolysis of all the ether bonds in the lignin. If one assumes the average molecular mass of a lignin monomer to be 166 g/mol and that 57% of the linkages in unmilled lignin are ether linkages (as indicated by NMR spectroscopy) a moisture content of 6.0 wt% would be required to cleave all the ether linkages. However, the maximum in yield of monomers produced occurred at 14% moisture. This represents a point at which enough water is supplied to the milling vessel to overcome any limiting effects for hydrolysis but not enough to cause significant plasticization. The discrepancy between the calculated minimum amount of water necessary and this result is likely related to non-perfect mixing of the solid system. Curiously, this maximum in monomeric yield did not correspond to a significant decrease in average relative molecular weight due to a decrease in dimer yield, but an increase in the yield of higher length chains. This suggests the increase in water leads to an increase in reactivity, and also that the dimers are converted into both stable monomers and unstable products that participate in condensation reactions.

By adding more water to the system, the average relative molecular weight after milling with sodium hydroxide could be lowered until reaching a moisture content of 20 wt%, where the average relative molecular weight increased again. Once at 20 wt% moisture, the amount of water in the system reached a point where the sample resembled a sludge rather than a powder, and effective grinding was no longer possible. Consequently, addition of excess water in the beginning of the reaction is impractical and can result in an overall reduction of yields. However, it is possible that the gradual addition of water to the system, such that the water in the system is never fully consumed, can ensure that plasticization does not limit the reaction. This will also likely alleviate condensation reactions that occur when water is depleted in the system.

2.5 Conclusions

Mechanochemistry offers a promising approach for the depolymerization of lignin in a solvent-free process close to ambient conditions. In the presence of sodium hydroxide, the molecular mass of lignin fragments can be reduced substantially within 10 min of milling. However, the effectiveness of depolymerization is limited by the formation of reactive intermediates that tend to undergo repolymerization reactions (e.g., condensation) that form products, which can be more difficult to depolymerize than original lignin. However, the addition of methanol as a scavenger can quench these reactions and allow for the formation of stable monomeric products. Moisture can have a similar effect, but the addition of excess water results in plasticization, so that effective milling becomes impossible. Thus, controlled addition of scavengers could be necessary to achieve the desired efficiency in mechanochemical processes for lignin conversion. Regardless of the nature of the scavenger, the most abundant monomeric products include phenol, 2,4,5-

trimethoxybenzaldehyde, syringol, and guaiacol. These products have similar molecular structures, making them an attractive stream for the production of aromatics.

CHAPTER 3. MECHANOCATALYTIC DEPOLYMERIZATION OF LIGNIN WITH SOLID ACID AND BASE CATALYSTS

3.1 Introduction

In order for lignocellulosic biomass to be chemically valorized into fuel precursors or fuels, its polymeric structure must be broken down. This can be accomplished through hydrolytic cleavage of linkage groups using an acid or base catalyst. Generally, base catalysts are more effective than acids at depolymerization of lignin, but can only facilitate the cleavage of ether linkages.[8] Acid catalysts have also been shown to hydrolytically cleave ether bonds, in addition to demonstrating the ability to cleave carbon-carbon bonds.[5] The possibility of carbon-carbon bond cleavage presents an opportunity for a more complete depolymerization than is possible with a base catalyst.

Strong acids like hydrochloric acid or sulfuric acid[98] and strong bases like sodium hydroxide[99] are particularly effective catalysts for facilitating hydrolytic depolymerization, but are difficult to recover once the reaction is completed. Such strong acids and bases are commonly left unrecovered altogether, and are factored into the cost of the process.[100] Using a solid acid or base catalyst to perform hydrolysis can alleviate this concern. By selecting a catalyst that is insoluble in the chosen solvent, in which the biomass reactant is dissolved, solid catalysts may be easily filtered and reused.[100] Thus, although a solid catalyst may convert lower yields than a strong acid or base, it may be more cost effective based on its ability to be recycled.

Under normal thermochemical conditions, solid-solid reactions are uncommon.[101] However, by supplying mechanical energy to a chemical system, such as grinding in a ball mill, solventless solid-solid interactions can occur.[12] Mechanochemistry has been shown to be effective for depolymerization of biomass in the presence of acid and base catalysts.[49, 50, 60] Numerous researchers have noted the effectiveness of using strong acids to break down cellulose into high yields of water-soluble oligomers through an impregnation method.[51-56] However, solid acid catalysts have also been shown to induce high conversions of cellulose into water-soluble oligomers, albeit with longer reaction times.[49, 50] Despite this, the ability to use a solid catalyst in a mechanochemical system presents an interesting opportunity for efficient catalyst recovery and recycling.

Although many researchers have investigated mechanochemical treatments of cellulose, mechanochemical reactions on lignin have been significantly less explored. Kleine et al. demonstrated the ability of β-O-4 linkages in lignin model compounds to be cleaved through strong-base catalyzed hydrolysis under mechanochemical conditions.[60] I have previously shown in Chapter 2 of this work that organosolv lignin can be rapidly depolymerized through mechanochemical treatment with sodium hydroxide, reaching nearly half its original relative molecular weight after only 30 minutes of milling. However, after these reactions with sodium hydroxide had progressed, neutralization with an acid was necessary before most analytical techniques could be successfully carried out. This indicates that some of the products of the reaction are sodium salts, arising from incomplete hydrolysis. This situation makes sodium hydroxide difficult to recover after the reaction is completed. In an industrial application, this could result in either an expensive catalyst

recovery process or the constant need for fresh catalyst for each pass. A more idealized process would make use of a catalyst that is easier to recover.

The purpose of this work is to test various solid catalysts for their effectiveness in mechanochemical depolymerization of lignin. Reactions were conducted with organosolv lignin and selected catalysts in a mixer mill in the absence of a solvent. Relative molecular weight analysis of reaction products was measured with Gel Permeation Chromatography (GPC). Yields of monomeric species were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). Finally, the ability of each catalyst to be recovered after being used in a reaction was recorded.

3.2 Experimental Section

3.2.1 Materials

Organosolv lignin from beech was obtained from Fraunhofer Institut in Leuna, Germany. Methanol (CHROMASOLV® for HPLC, ≥99.9%), tetrahydrofuran (ACS reagent, >99.0%), Magnesium Oxide (≥99, trace metals basis), and 3,5 dimethoxyphenol (99%) were purchased from Sigma-Aldrich. Magnesium hydroxide (95–100.5%) was obtained from Alfa Aesar. Samples of mordenite (Si/Al = 10) and ZSM-5 (Si/Al = 25) were purchased from Zeolyst. Synthetic hydrotalcite was obtained from Beantown Chemical. Kaolin samples (A, B) were donated by Imerys.

3.2.2 Mechanochemical Reactions

Ball-milling of lignin was performed in stainless steel vessels (25 mL) using a Retsch MM400 ball mill at room temperature. The vessels were equipped with three

milling balls each (12 mm diameter, stainless steel). The ball-milling was carried out at 800 rpm (13.3 Hz) for 0 to 8 hours. To avoid overheating at long milling times, the mill was stopped for 10 minutes after every 30 minutes of milling. For all tests, the milling vessel was filled with organosolv lignin (1.50 g) and a solid acid or base catalyst (1.50 g).

3.2.3 Catalyst Recovery

To determine the degree of recovery for each catalyst used in this work, reaction products were dissolved in methanol and vacuum filtered using 0.2 μm quantitative filters. After drying at 100 °C for 24 hours, the leftover catalyst on the filter was weighed.

3.2.4 Gas Chromatography – Mass Spectrometry (GC-MS)

The milled samples were dissolved in methanol and diluted to a concentration of 10 mg/mL. 3,5-Dimethoxyphenol was added as an internal standard. Samples were filtered using 0.2 μm polypropylene membranes. GC-MS analysis was performed using a Varian (Agilent) 450-GC with a FactorFour™ VF-35ms capillary column (30m x 0.25mm x 0.25μm) coupled with a 300-MS Varian (Bruker) mass spectrometer (EI, 200 °C). The carrier gas was helium at 1.0 mL/min with an autosampler injection volume of 1.0 μL. The temperature of the column was initially held at 70.0 °C for 1.50 minutes, then raised at a rate of 35.0 °C/min to 100.0 °C. The temperature of the column was then raised at a rate of 10 °C/min to 300.0 °C, where it was held for 12.0 min.

Yield of total detected monomeric species was calculated as follows:

$$yield\ (wt\%) = \frac{m_{volatile\ monomers}}{m_{total\ reacted\ sample}} * 100\% \quad (3)$$

It is important to note that GC-MS is not strictly quantitative, and the detector in an MS responds differently for each compound based on the fragmentation reactions that occur during the analysis. Fortunately, most of the detected products were substituted aromatic compounds with similar molecular structures. These compounds generate similar fragmentation patterns in their mass spectra, and thus, differences in their response factors are assumed to be minimal enough to obtain reasonable estimates of their concentration. Consequently, the internal standard that was chosen is an isomer of one of the most prominent products analyzed to reduce discrepancies in the response factor.

3.2.5 Gel Permeation Chromatography (GPC)

The milled samples were dissolved in THF and diluted to a concentration of 4 mg/mL. Samples were filtered using 0.2 μm Nylon membranes. An amount of 1.0 μL of each sample was injected into an Agilent PL-GPC-50 with a Refractive Index Detector. THF was used as an eluent with a flow rate of 1.0 mL/min, and polystyrene standards were used for calibration. The data was analyzed using Cirrus GPC software (Version 3).

3.3 Results and Discussion

3.3.1 Catalyst Selection

Seven catalysts were tested for their ability to mechanocatalytically depolymerize lignin in this work. These included two acidic zeolite catalysts from Zeolyst, ZSM-5 and

mordenite, which possess aluminosilicate microporous structures. The acidic kaolin samples have layered aluminosilicate structures. Magnesium hydroxide consists of a basic layered hydroxide structure, while a synthetic Mg-Al hydrotaclite obtained from Beantown Chemical possesses a basic layered double hydroxide structure. Finally, magnesium oxide is comprised of a slightly basic cubic crystal structure.

3.3.2 Catalyst Recovery

After each reaction, the products from the lignin reaction were dissolved in methanol and vacuum filtered to recover the respective catalyst. For each sample, the entire catalyst was recovered using this method, within an error of ±1%. This result is in contrast to the use of sodium hydroxide in my previous work, detailed in Chapter 2, which could not be recovered in this manner. This high degree of recoverability is highly desirable for potential application in an industrial mechanocatalytic process. It is important to note that this method of measuring catalyst recovery does not take into account any insoluble lignin surface deposits that may be left on the surface of the catalyst. Additionally, drying at 100 °C may not remove methanol that has been strongly adsorbed to the catalyst surface. Evidence of lignin deposits or adsorbed methanol could potentially be obtained in future work through analysis of the recovered catalysts with infrared spectroscopy.

3.3.3 Solid Acid Catalysts

Four solid acid catalysts were tested for their ability to depolymerize lignin under mechanocatalytic conditions. Figure 9 shows the number average molecular weight (M_n) as a function of milling time, relative to a standard calibration of narrow polystyrene standards. Samples of uncatalyzed lignin exhibited minimal changes in relative molecular

weight over the milling times tested. When a solid acid was added to the reaction vessel, small changes in molecular weight could be observed. Samples milled with kaolin B and ZSM-5 underwent a decrease of more than 50 g/mol within the first hour of milling, stabilizing at approximately 700 g/mol. Mordenite-catalyzed samples displayed a slower decrease in molecular weight, reaching approximately 700 g/mol after 5 hours of milling. It should be noted that the standard error bars calculated for these sets of data are nearly as large as the recorded differences between the initial and final molecular weights, thus calling into question the statistical significance of these results. Despite this, the observed relative molecular weights of the acid catalyzed samples were consistently lower than the uncatalyzed sample, indicating that some degree of depolymerization occurred.

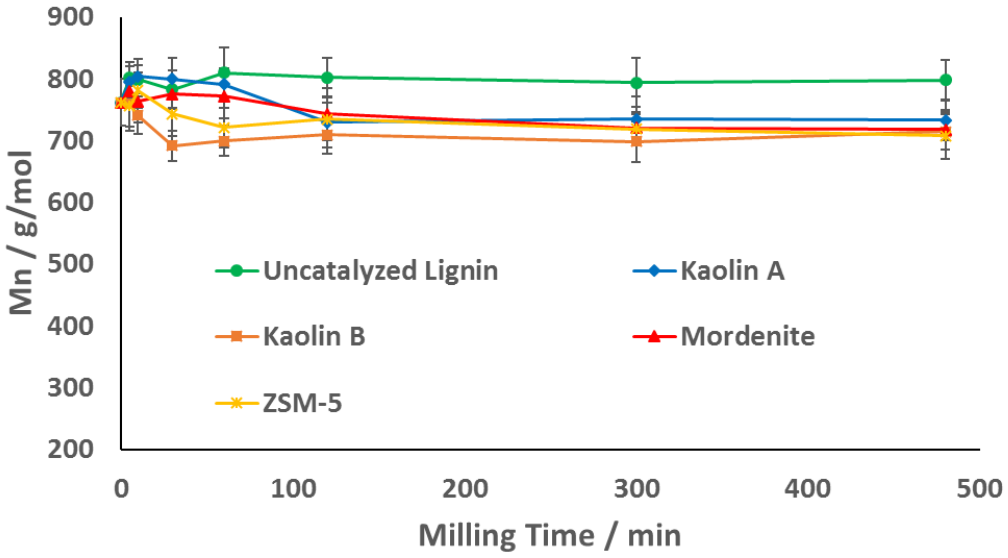

Figure 9: Number average molecular weight (M_n), as determined by GPC, plotted as a function of milling time. Samples of 3.00 g uncatalyzed lignin and mixtures of 1.50 g lignin combined with 1.50 g of a solid acid catalyst were milled in a mixer ball mill at 800 rpm.

The yields of monomeric compounds produced from reactions with these solid acid catalysts were estimated using GC-MS (Figure 10). The milled uncatalyzed lignin showed no statistically significant change from the 3.23 wt% monomer content of the unmilled sample up to eight hours of milling. Likewise, the yields for each solid acid catalyzed system appears to be uncorrelated to milling time, with little variation from the monomer content of the original unmilled lignin sample.

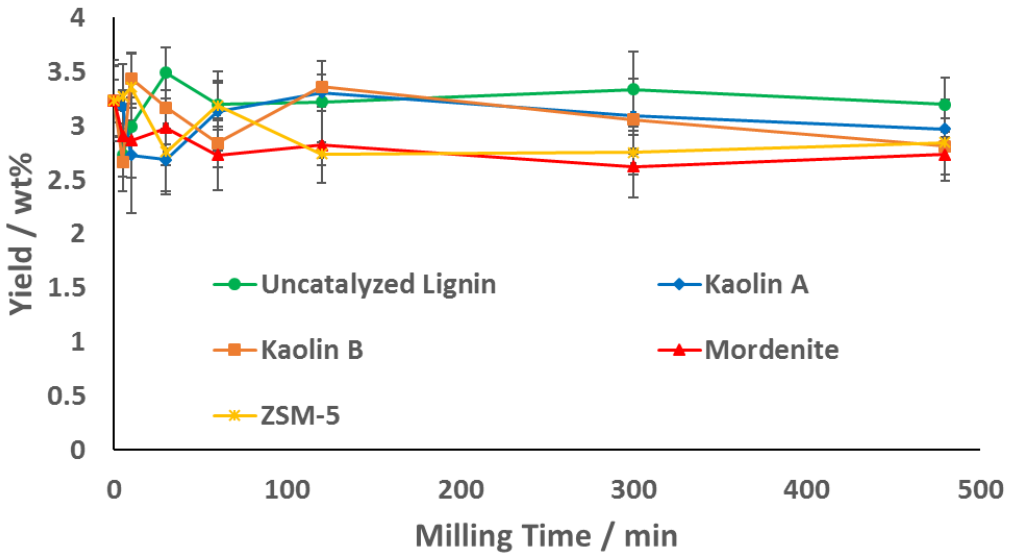

Figure 10: Yield of monomeric species produced, as determined by GC-MS, plotted as a function of milling time. For these experiments, samples of 3.00 g uncatalyzed lignin and mixtures of 1.50 g lignin combined with 1.50 g of a solid acid catalyst were milled in a mixer ball mill at 800 rpm.

By comparing the relative molecular weight data as determined by GPC with the yields of monomers detected by GC-MS, it appears that the solid acid catalysts are unsuited for mechanocatalytic depolymerization of lignin. It is possible that attempting to activate the catalysts through calcination prior to performing reactions might lead to depolymerization. However, experiments of mechanocatalytic depolymerization reactions

of cellulose using solid acid catalysts, including kaolin and zeolites, have been proven to be fairly efficient at producing high yields of water soluble oligosaccharides without the use of a calcination step.[50] These depolymerization reactions of cellulose also involved the hydrolytic cleavage of an ether bond, which indicates that some other factor may be limiting depolymerization reactions in lignin. It is possible that the large, crosslinked, three-dimensional structure of lignin prevents the molecules from reaching the pores of the catalysts, where the highest abundance of active sites should be present.[102] However, kaolin is a layered silicate material that has been shown to delaminate through ball milling, dramatically increasing its available surface area. Some researchers have speculated that the impact force of ball milling can induce conformational changes in the linear structure of cellulose into an activated state that is more suitable to interact with active sites on a catalyst.[76] The crosslinked structure of lignin is less capable of deformation into an activated state, and thus is less likely to interact with active acid sites on the material.[103] It is important to note that there is consistent evidence that carbohydrates are more easily broken down by acids than lignin, although thermochemical acid-catalyzed lignin depolymerization is still a common technique.[104]

3.3.4 Solid Basic Catalysts

In addition to the solid acid catalysts studied in the previous section, several solid basic catalysts were tested for their ability to mechanocatalytically depolymerize lignin. As seen in Figure 11, synthetic hydrotalcite (HTC) and magnesium oxide (MgO) had only a small effect on the relative molecular weight of lignin when milled for up to eight hours. The approximate decrease by 50 g/mol after eight hours of milling is reminiscent of the solid acid catalysts tested. As with the solid acid catalysts, the standard error bars prevent

the slight decrease in molecular weight from being statistically significant. However, milling with magnesium hydroxide ($Mg(OH)_2$) showed a larger impact on the molecular weight of the lignin sample. After incremental decreases in relative molecular weight over the first hour of milling, the depolymerization appeared to increase, dropping to approximately 580 g/mol after five hours of milling. After this point, depolymerization slowed, reaching approximately 560 g/mol by eight hours of milling.

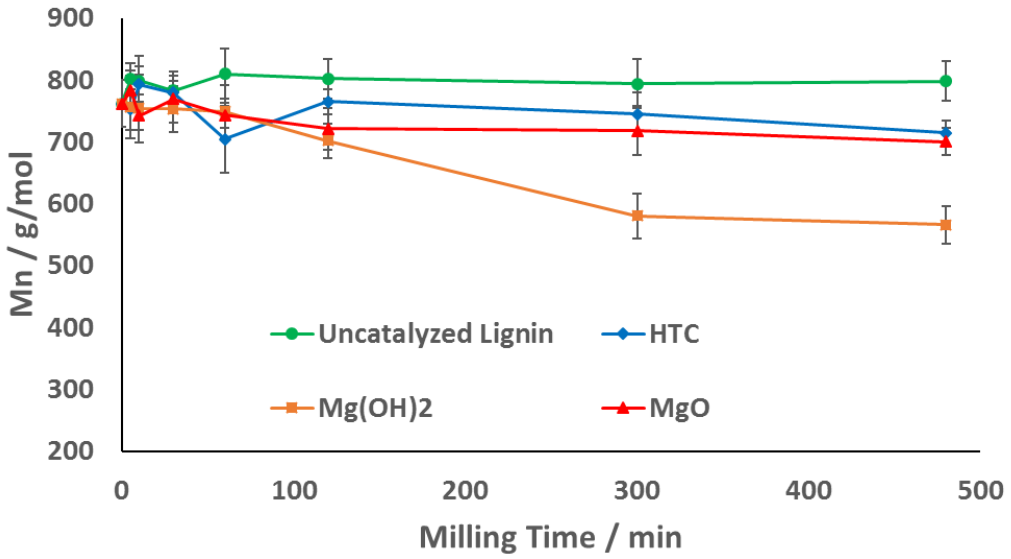

Figure 11: Number average molecular weight (M_n), as determined by GPC, plotted as a function of milling time. Samples of 3.00 g uncatalyzed lignin and mixtures of 1.50 g lignin combined with 1.50 g of a solid base catalyst were milled in a mixer ball mill at 800 rpm.

Examining the yield of monomeric species detected by GC-MS revealed similar information. As seen in Figure 12, samples milled with HTC and MgO resulted in minimal changes from the original 3.23 wt% of monomer content of the lignin. However, samples milled with $Mg(OH)_2$ showed a maximum monomer yield of approximately 6.35 wt% after one hour of milling. Beyond one hour of milling, the monomer yield drops slightly to

values between 5 and 6 wt%. The monomer yield produced by reactions with $Mg(OH)_2$ does not reach the values reported previously in Chapter 2 of my work for milling with NaOH, including the maximum of 24.90 wt% after milling for five hours. Despite this, reaction products after milling with $Mg(OH)_2$ do not require neutralization with an acid before being analyzed, unlike those milled with NaOH. Attempting the same neutralization protocol as detailed in Chapter 2 of my work resulted in no change in either relative average molecular weight or yield of monomeric species. This allows the $Mg(OH)_2$ to be completely recovered via filtration after dissolving the reaction products in a solvent, a key advantage over using NaOH as a mechanocatalyst.

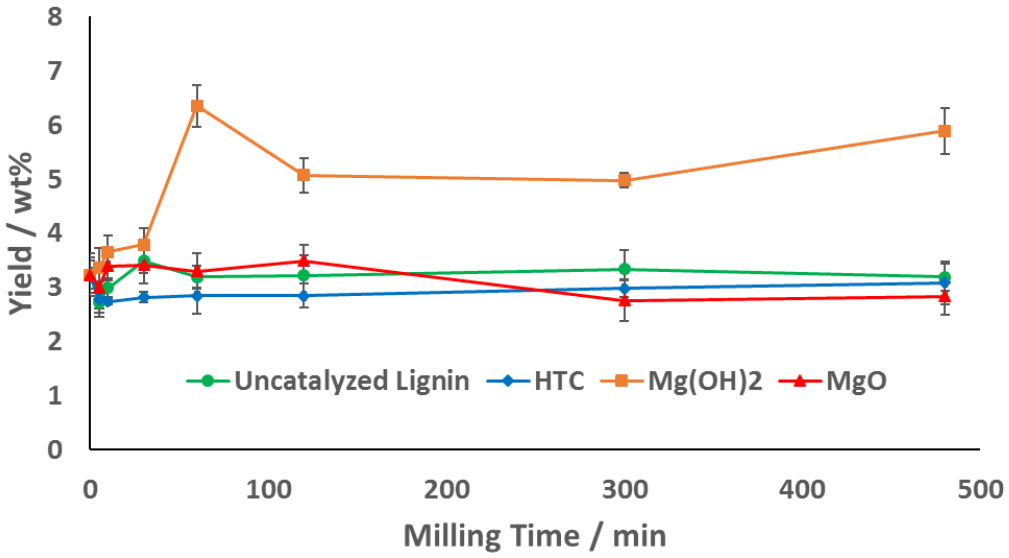

Figure 12: Yield of monomeric species produced, as determined by GC-MS, plotted as a function of milling time. For these experiments, samples of 3.00 g uncatalyzed lignin and mixtures of 1.50 g lignin combined with 1.50 g of a solid base catalyst were milled in a mixer ball mill at 800 rpm.

Out of all the solid acid and base catalysts tested in this study, only $Mg(OH)_2$ was able to successfully reduce the molecular weight of lignin by a statistically significant

amount and also produce monomeric species in notable quantities. The cubic crystal structure of MgO appears to be unable to efficiently interact catalytically with lignin molecules.[105] However, $Mg(OH)_2$ is comprised of a layered hydroxide surface similar to the acidic kaolin.[106] Delamination of the $Mg(OH)_2$ sheets could produce a high surface area with active basic sites, which may be more suitable for mechanocatalytic lignin depolymerization, unlike the acid sites of kaolin. This could be confirmed in future work through surface area analysis using nitrogen physisorption, and by characterizing and quantifying active sites using CO_2 chemisorption for basic sites and pyridine chemisorption for acidic sites. HTC is also a layered hydroxide material, yet it does not display the same mechanocatalytic activity as $Mg(OH)_2$.[107] It is possible that this inactivity is caused by chemical changes to the catalyst induced by the high energy impacts of ball milling. It has been shown that HTC can degrade into catalytically inactive MgO/Al_2O_3 spinel when exposed to temperatures above 760 °C.[108] Given that ball milling is theorized to create 'hot spots' that can exceed 1000 °C that last 10^{-3} to 10^{-4} s, it is possible that HTC may degrade in the reaction conditions of the given experiment.[11, 14] This hypothesis could be verified in a future study.

3.4 Conclusions

In this work, several solid acid and base catalysts were tested for their ability to depolymerize organosolv lignin under mechanocatalytic conditions. Relative average molecular weights from milling times up to eight hours were analyzed by GPC. Additionally, yields of monomeric species of the same samples were identified and quantified by GC-MS. None of the tested solid acid catalysts were able to affect the average molecular weight or content of monomeric species of the milled samples. Of the sold base

catalysts tested, only $Mg(OH)_2$ showed any statistically significant ability to reduce the molecular weight of lignin samples and produce monomeric species in quantifiable amounts. A concrete explanation for the success of $Mg(OH)_2$ over the other catalysts tested in this study requires more evidence, but it is possible that its layered hydroxide structure offers advantages over porous structured alternatives. Though not as effective at mechanocatalytic depolymerization as NaOH has proven, $Mg(OH)_2$ offers significantly easier catalyst recovery, which could be beneficial to application to industrial processes.

CHAPTER 4. MECHANOCATALYTIC HYDROGENATION OF DIPHENYL ETHER

4.1 Introduction

Depolymerization of lignin generally results in monomers and oligomers made from functionalized aromatic species.[5, 8] However, these structures typically possess lower heating values and volatilities while having higher acidities and viscosities than petroleum-derived oils.[109-112] These differences are often related to the higher oxygen content and unsaturated rings of the lignin-derived species. Both of these issues may be solved through reactions with hydrogen. Hydrogenation can effectively saturate alkenes and aromatic rings.[113] Hydrogenolysis can split oxygen-containing ether bonds.[114, 115] Finally, hydrodeoxygenation can remove oxygen-containing functional groups.[116, 117] All three of these reactions can be performed with heterogeneous catalysts. However, they frequently require high hydrogen pressures and temperatures to produce high yields of products.[116, 118]

Due to the high complexity of lignin molecules, studies of hydrogenation, hydrogenolysis, and hydrodeoxygenation are typically studied for lignin model compounds, which include monomers, dimers, and other small oligomers that represent common motifs in the structure of lignin.[116] Dimers are often chosen as a feedstock for studies of these reactions, because they can undergo all three types of reactions, while being simple enough to minimize the total number of possible products.[113-121] For

example, diphenyl ether can undergo any of the reactions shown in Figure 13 when in the presence of a supported metal catalyst and hydrogen gas.[118]

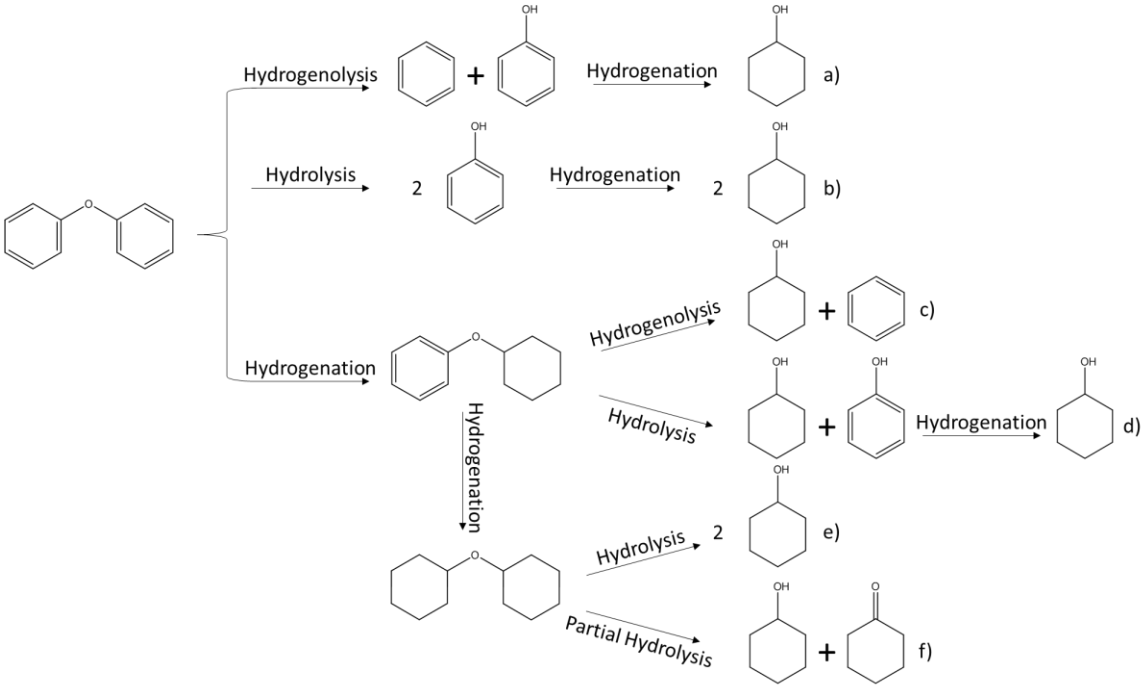

Figure 13: Reaction scheme for diphenyl ether when in the presence of a supported metal catalyst and hydrogen gas, as proposed by He et al.[118]

It has been shown previously in Chapters 2 and 3 of my work that lignin can be hydrolytically depolymerized under mechanochemical conditions in a ball mill. This process allowed for performing the reaction efficiently at ambient temperatures and pressures and without the need for a solvent. Solventless processes are ideal for lignin, due to its poor solubility in most conventional solvents.[5] Most hydrogen-upgrading reactions on lignin products are performed as a downstream process, after the smaller lignin oligomers can be retrieved through dissolution in a solvent.[8] However, a one-pot process for depolymerization and hydrogen-upgrading of lignin can be imagined through the implementation of performing both reactions simultaneously under mechanochemical

conditions. This approach may also provide benefits in the separation of products from unreacted material and catalysts. The hydrogenated products will exhibit higher volatility than the unreacted material,[109] and can potentially be carried out of the reactor with the flowing hydrogen stream. This would leave unreacted material and the catalysts inside the reactor, while the hydrogenated products can be collected in a condenser downstream.

Mechanochemistry has been shown to have the ability to drive a variety of traditionally thermochemical organic chemical reactions.[14, 36-39, 42-44, 46] Despite this, evidence of gas phase mechanochemical reactions is limited to a single study on solid-catalyzed carbon monoxide oxidation inside a ball mill.[122] Using modified milling equipment, the authors of this study were able to introduce a gas stream of carbon monoxide into an active ball mill. Using the results of this study, the authors were able to prove that the energy input from the ball mill was satisfactory to drive the necessary reaction without any additional heating or pressure. Therefore, it is reasonable to hypothesize that hydrogenation reactions may also be possible under mechanochemical conditions.

The purpose of this work is to investigate the ability of hydrogenation and hydrodeoxygenation reactions to occur under mechanochemical conditions. A specialized milling reactor with an inlet and an outlet for a gas stream was designed for the purposes of conducting experiments under a hydrogen atmosphere. Mechanochemical reactions between diphenyl ether and hydrogen were carried out using platinum supported on alumina (Pt/Al_2O_3) as a catalyst. Products of the reaction were identified and quantified by gas chromatography-mass spectrometry (GC-MS).

4.2 Experimental Section

4.2.1 Materials

Diphenyl ether (99%) and Benzyl phenyl ether (97%) were obtained from Alfa Aesar. Pt/Al_2O_3 (5 wt% platinum) was purchased from Sigma Aldrich. Dichloromethane (HPLC grade, 99.9%) was obtained from Acros.

4.2.2 Mechanochemical Reactions

Ball-milling reactions were performed in a modified stainless steel vessel (50 mL) using a Retsch MM400 ball mill at room temperature. Changes made to the milling vessel were inspired by the work of Immohr et al.[122] The milling vessel was modified from its original configuration to add an inlet and outlet to accommodate a gas flow. Both the added inlet and outlet contained a stainless steel frit to contain solid matter within the vessel. The inlet and outlet were connected to Swagelok ball valve fittings. The screw cap of the milling vessel was fitted with a Viton O-ring from McMaster Carr to ensure an airtight seal. The modified vessel is shown in Figure 14. An Omega 2604A mass flow controller supplied a gas flow of 50.00 SCCM to the inlet of the vessel at atmospheric pressure. At the outlet, a cold finger condenser was placed in an ice water bath to trap products that were carried out of the reactor by the gas flow. The modified reactor set up is shown in Figure 15.

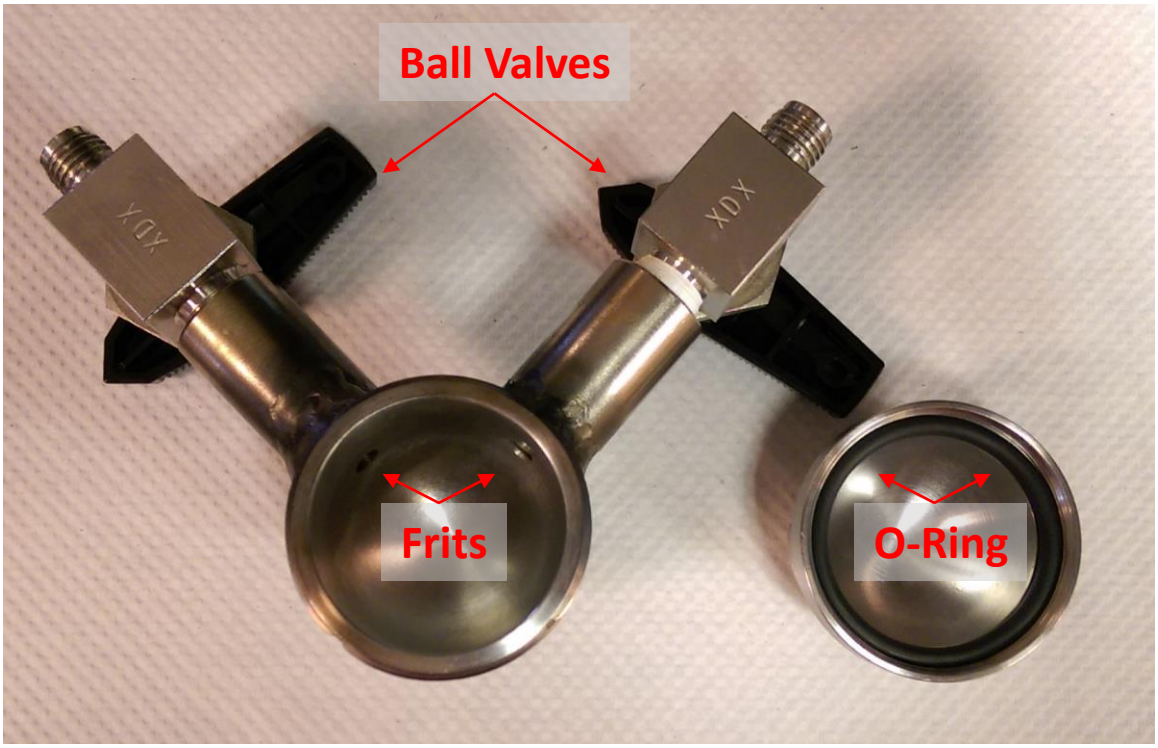

Figure 14: Modifications to the 50 mL milling vessel included an inlet and an outlet fitted with frits and Swagelok ball valves, and an o-ring to ensure an air-tight seal.

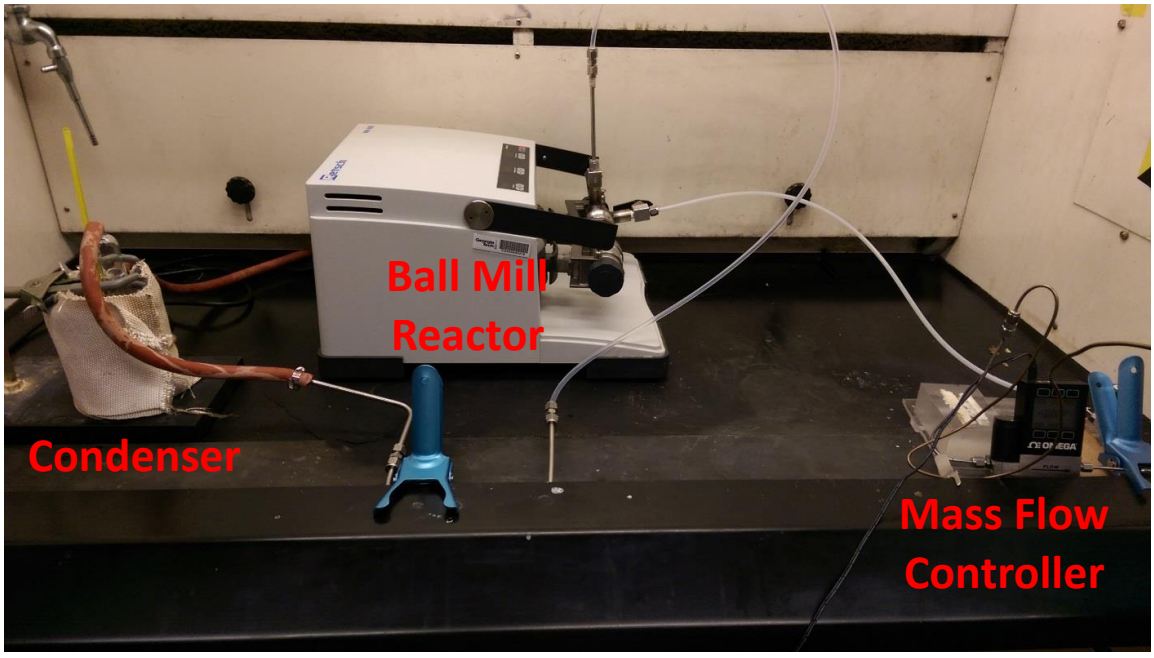

Figure 15: The gas flow milling reactor setup, including a mass flow controller, modified milling vessel with an inlet and outlet, and cold finger condenser.

The vessels were equipped with six milling balls each (12 mm diameter, stainless steel). The ball-milling was carried out at 800 rpm (13.3 Hz) for 0 to 8 hours. For all tests, the milling vessel was filled with diphenyl ether (5.75 g) and Pt/Al_2O_3 catalyst (0.25 g). Before each reaction, the reactor was purged with nitrogen gas at 50 SCCM for 15 minutes, and again with hydrogen gas at 50 SCCM for 15 minutes. All reactions were carried out with a flow of hydrogen gas at 50 SCCM.

4.2.3 Gas Chromatography – Mass Spectrometry (GC-MS)

The milled samples were dissolved in dichloromethane and diluted to a concentration of 10 mg/mL. Benzyl phenyl ether was added as an internal standard. Samples were filtered using 0.2 μm polypropylene membranes. The condensate that accumulated in the cold finger after each reaction was collected by washing with 10 mL of dichloromethane. GC-MS analysis was performed using a Varian (Agilent) 450-GC with a FactorFour™ VF-35ms capillary column (30m x 0.25mm x 0.25μm) coupled with a 300-MS Varian (Bruker) mass spectrometer (EI, 200 °C). The carrier gas was helium at 1.0 mL/min with an autosampler injection volume of 1.0 μL. The temperature of the column was initially held at 30.0 °C for 5.00 minutes, then raised at a rate of 10.0 °C/min to 120.0 °C. The temperature of the column was then raised at a rate of 45.0 °C/min to 250.0 °C, where it was held for 12.0 min.

Yields of detected reaction product species were calculated based on carbon content, as follows:

$$yield\ (mol\%) = \frac{mol_{C\ in\ product\ species}}{mol_{C\ in\ initial\ diphenyl\ ether}} * 100\% \quad (4)$$

Conversion of diphenyl ether was calculated as follows:

$$conversion\ (mol\%) = \frac{mol_{C\ in\ initial\ diphenyl\ ether} - mol_{C\ in\ unreacted\ diphenyl\ ether}}{mol_{C\ in\ initial\ diphenyl\ ether}} * 100\% \quad (5)$$

It is important to note that GC-MS is not strictly quantitative, and the detector in an MS responds differently for each individual compound measured by the instrument. Fortunately, the detected products consisted of compounds with similar overall molecular structures. These compounds generate similar fragmentation patterns within the MS and thus differences in the response factor between them could be assumed to be minimal enough to obtain rough quantification estimates. For the same reason, an internal standard of benzyl phenyl ether was chosen in order to reduce discrepancies in response factor due to its structural similarities to diphenyl ether and its resulting reaction products. However, future work should verify these results using GC-FID analysis, which provides much more accurate quantification.

4.3 Results and Discussion

Figure 16 displays the yield of each detected product of the mechanocatalyzed hydrogenation of diphenyl ether as well as the conversion of diphenyl ether as a function

of milling time, as measured by GC-MS. The only three detectable products of the reaction were dicyclohexyl ether, cyclohexanol, and cyclohexanone. The yields of all three products were low for the first hour of milling, but after two hours of milling, a large increase in the yields of dicyclohexyl ether and cyclohexanol was observed. Between two and eight hours of milling, the yield of cyclohexanol continued to increase, while the yield of dicyclohexyl ether slightly decreased. The conversion of diphenyl ether also rose sharply after two hours of milling, and continued to increase up to eight hours of milling. Through comparison of the diphenyl ether conversion and product yield results, the extent of closure in the mass balance of carbon can be determined. Between 5 minutes and 1 hour of milling, the carbon balance was closed to within 0.01%. After two hours of milling, this discrepancy rose to 1.1%, and rose to 2.6% after 8 hours of milling. In all cases, the calculated conversion of diphenyl ether was higher than the sum of the product yields. Therefore, the missing carbon at these higher milling times may have been lost through experimental error in analysis using the GC-MS for quantification, or due to the cold trap not having a low enough temperature to properly condense all the product leaving the reactor.

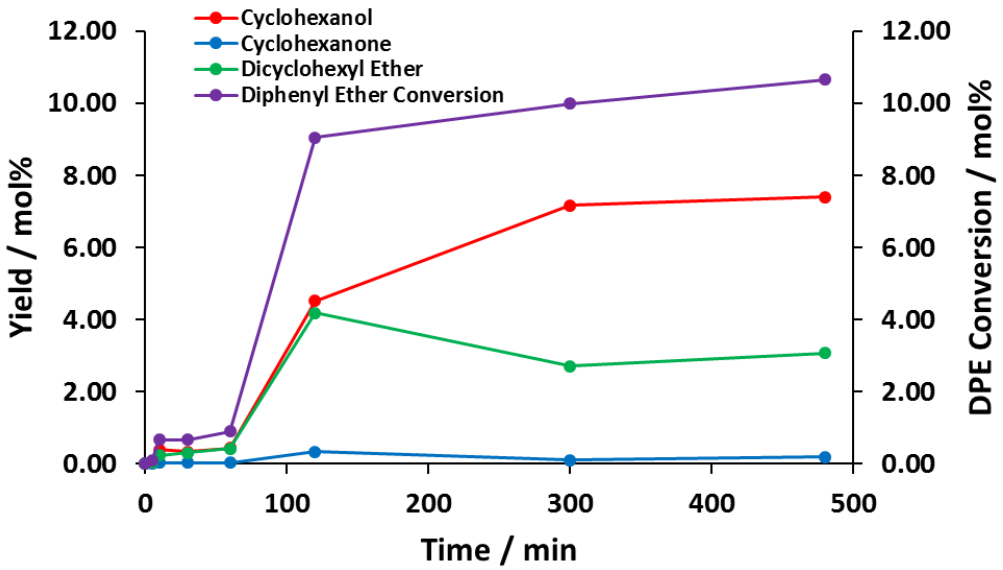

Figure 16: Product yields (on a C atom basis) and diphenyl ether conversion, as determined by GC-MS, plotted as a function of milling time. Mixtures of 5.75 g of diphenyl ether combined with 0.25 g Pt/Al_2O_3 were milled at 800 rpm under a gas flow of 50 SCCM of hydrogen gas.

The shape of the diphenyl ether conversion curve is notable, given that there appears to be a large increase between one and two hours of milling, followed by a more gradual increase afterwards. This result is reminiscent of the work of Immohr et al., in which carbon monoxide was mechanocatalytically oxidized to carbon dioxide using a variety of metal oxide catalysts. [122] The authors noted low initial conversions, followed by a large increase in conversion between two and five hours of milling. One hypothesis put forward to explain this is that the mechanocatalytic milling requires an activation period driven by the grinding of the catalyst. Specifically, the Pt/Al_2O_3 used in the current work possibly requires the energy from the mechanical impact of the milling to efficiently reduce the catalyst in the hydrogen atmosphere of the reactor. This could be confirmed in future work by reducing the catalyst in a calcining oven prior to the reaction. Another possible explanation for this result is the potential for physical deformation of the catalyst surface

by the impacts in the ball mill, which may create highly active defect sites. Future work should include characterization of active sites before and after milling, to determine whether impacts in the ball mill can significantly alter the surface of the catalyst.

The observed products of dicyclohexyl ether, cyclohexanol, and cyclohexanone provide potential insights into the pathway of the hydrogenation reaction of diphenyl ether. The absence of phenol or benzene as products indicate that hydrogenation of the aromatic rings of diphenyl ether into dicyclohexyl ether occurs before the ether bond is cleaved. Additionally, the absence of cyclohexane as a product suggests that ether cleavage is carried out not through hydrogenolysis but instead through hydrolysis with the water present in the moisture content of the diphenyl ether sample. Hydrolytic cleavage could explain the absence of oxygen free products that would have to be present if the ether bond was cleaved by hydrogenolysis. This hypothesis should be tested in future work by investigating the effects of adjusting the amount of water present in the system on the yields of observed products. The absence of cyclohexane also indicates that hydrodeoxygenation does not seem to take place under the given conditions. Based on the observed products, it would appear that the reaction follows a combination of the pathways e) and f) as defined by Figure 13.

It is possible that benzene or cyclohexane are generated in the reactor, but are not appropriately collected in condenser. The condenser used for this work was placed in an ice water bath with sodium chloride, reaching a temperature of approximately -10 °C. By using a bath of dry ice and acetone, it would be possible to reach bath temperatures of around -78 °C, which may recover products which previously were lost in the gas stream. Alternatively, the reaction conditions may not be harsh enough for hydrogenolysis or

hydrodeoxygenation to occur. This may be investigated in future work by supplying more energy to the system, either by increasing the milling speed or increasing the temperature of the reactor. Hydrodeoxygenation may also be limited by the Pt/Al_2O_3 catalyst, which may not possess acid sites strong enough to perform the dehydration step of the reaction. Thus, testing of additional catalysts with stronger acid sites should be included in future work. Finally, future work should test this reaction on a larger variety of model compound feedstocks which more closely approximate the structure of lignin oligomers. The structure of lignin is diverse, and oligomers made from various aromatic compounds may follow different reaction pathways than diphenyl ether under the same conditions.

4.4 Conclusions

In this work, a reactor was designed for the purposes of performing hydrogenation reactions under mechanocatalytic conditions. Diphenyl ether was reacted in the modified ball milling vessel under a hydrogen atmosphere at ambient temperature and atmospheric pressure to produce dicyclohexyl ether, cyclohexanol, and cyclohexanone. These products indicate that the reaction pathway likely includes ring hydrogenation followed by a hydrolytic cleavage of the ether bond. The absence of cyclohexane and benzene suggest that hydrogenolysis and hydrodeoxygenation do not occur under the current reaction conditions. However, it is possible that these reactions do occur, but are not captured in the current condenser conditions. This would explain the discrepancies in the carbon balance seen at high milling times. Based on these promising preliminary results, the reactor setup designed for this work could be used for a variety of future experiments involving mechanocatalytic reactions under varying atmospheres.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Mechanochemical Depolymerization of Lignin and Quenching of Reactive Intermediates

The results of this work demonstrate the potential of mechanochemical reactions for lignin depolymerization. Organosolv lignin can be depolymerized by milling with sodium hydroxide. Most of the reaction occurred within the first 30 minutes. The process was driven purely through mechanical energy, and thus did not require elevated temperatures or pressures. Additionally, this method removes the need for a solvent typically necessary for thermochemical hydrolysis reactions of lignin. The results also showed obvious limitations in the extent depolymerization can occur, due to non-ether linkages, repolymerization reactions, and limiting reactants. While strategies to alleviate the effects of some of these limitations have been addressed in the current work, there exist a variety of opportunities to continue this work.

While sodium hydroxide is effective at cleavage of ether bonds, these are not the only important linkages present in lignin. Carbon-carbon bonds cannot be cleaved by sodium hydroxide, and were therefore left unmodified in the reactions of the present work. However, some acid catalysts, such as zeolites ZSM-5 and mordenite,[123] have proven to be able to cleave these carbon-carbon linkages in lignin.[5, 8] Future work should include experiments with strong solid acids to determine the ability of these catalysts to cleave carbon-carbon linkages under mechanochemical conditions. A solid catalyst that is insoluble in organic solvents would also present the benefit of providing an easier separation from reaction products than sodium hydroxide, which required neutralization

before any analytical techniques could be performed. A variety of solid acid and base catalysts were tested for their ability to mechanocatalytically depolymerize lignin in Chapter 3 of this work. Reactions may also be run with multiple catalysts of different natures at once (e.g. sodium hydroxide and zeolite), to determine if there is a potential synergistic effect between the higher effectiveness of base catalysts and the ability of acid catalysts to cleave carbon-carbon bonds. Specifically, the use of solid catalysts will allow for acid-base pairs that will not neutralize each other, due to the support structures of each catalyst preventing contact of active sites.[124, 125]

This work showed the positive effects of increasing the water content or adding methanol as supplementary reactants for lignin depolymerization, including achieving lower average molecular weights and higher yields of monomers. However, future work should include a more robust comparison between the effects of water and methanol, to determine the differences in effectiveness of each reactant. This will be accomplished through two separate studies. First, reactant amount will be held constant for milling times between five minutes and eight hours. Second, reactant amount will be varied for a single milling time point. In this way, the ability of each reactant to lower the average molecular weight and to produce monomers can be directly comparable.

As seen in the present work, key disadvantage of increasing the water content of the system was the evidence of plasticization, which limited the effectiveness of the grinding in the ball mill. Addition of methanol may result in lower plasticization effects, due to weaker hydrogen bonding than exhibited by water.[126] Another idea is to control the addition of reactant, rather than supplying it all at once prior to the reaction, in order to

minimize any plasticization effects. This may be accomplished by introducing the reactant in a carrier gas stream into the reactor setup described in Chapter 4.

5.2 Mechanocatalytic Depolymerization of Lignin with Solid Acid and Base Catalysts

The second portion of this work involved a study of mechanocatalytic depolymerization of lignin using several solid acid and base catalysts. Of the seven catalysts tested, only magnesium hydroxide was effective for mechanochemical depolymerization of lignin. Despite this, there are many other classes of solid catalysts that may be tested for their ability to mechanocatalytically depolymerize lignin. Additional solid acid catalysts include sulfated zirconia, which is considered a superacid,[127] and transition metal oxides, such as nanosheets of niobium molybdate, which have demonstrated ability for thermochemical hydrolysis of biomass under conditions where zeolites were inactive.[128, 129] Other solid base catalysts which could be tested include supported alkali metal alumina or silica[130] and metal oxynitrides,[131] which would provide catalysts with similar high-surface area layered structures as kaolin or hydrotalcite, but with different active sites. Solid oxidative catalysts may also be considered, such as ceria zirconia or polyoxometalates, which have both been shown to depolymerize lignin under thermochemical conditions.[98] A larger sample of catalysts that are active for this reaction will allow for a deeper understanding of what factors influence the effectiveness of mechanocatalysts.

Based on the current work, it appears that basic catalysts are more effective at mechanocatalytic depolymerization of lignin. However, commercial hydrotalcite proved

to be ineffective, possibly due to low stability at high temperatures provided by 'hot spots' in the ball mill. Future work should investigate if the hydrotaclite structure degrades into spinel at the present reaction conditions, which would help explain the inactivity of the catalyst. Modified hydrotalcites with greater thermal stability, such as those ion-exchanged with CO_3^{2-}, may prove to be more catalytically effective than the unmodified commercial catalyst.[132]

Additional work should include characterization of the catalysts tested, including surface area, strength of active sites, and pore size, if applicable. Generally, catalysts with higher surface areas and stronger active sites are more active.[133] The pore size of the catalysts may limit the reaction if the lignin molecules are too large to effectively diffuse and adsorb.[134] Ball milling has been shown to increase values of surface area, strength of active sites, and pore size for some catalysts,[14] yet decrease these values for other catalysts.[135] However, the mechanisms behind these structural changes are currently not well understood.[14] Characterization should be done both before and after reactions, to determine which transformations increase or decrease the activity of specific catalysts in mechanocatalytic reactions. Reuse of recovered catalysts may be attempted to measure recyclability. Combinations of catalysts may also be tested, to determine if synergistic effects between solid acid and base catalysts can occur. Finally, the effects of adding supplementary water or methanol to the reaction system should be tested. In Chapter 2 of this work, it was determined that the addition of water or methanol to a sodium hydroxide catalyzed system resulted in lower average molecular weights and increased monomer production. This relationship should be true for other catalysts as well, and should be tested for all mechanocatalytic systems investigated in future work.

5.3 Mechanocatalytic Hydrogenation of Diphenyl Ether

For the final section of this work, a modified milling reactor was constructed in order to supply a gas flow of hydrogen during mechanocatalytic reactions. The modified reactor built for this work presents a variety of opportunities for the field of mechanocatalysis. The results of this work show the ability of the reactor to provide an environment for solvent-free hydrogenation reactions of the lignin model compound diphenyl ether at ambient temperature and pressure. However, this only represents the first application for what the reactor may be capable of. The hydrogenation reactions may be improved by testing of catalysts with a more acidic support to perform the dehydration step in hydrodeoxygenation than the Pt/Al_2O_3 used in the current work. In particular, the use of the combination of catalysts Pd/C and ZSM-5 has been shown to convert 100% of diphenyl ether to cyclohexane with 100% selectivity in water at 200 °C.[136] Future work should also include the testing of a variety of model compounds, in order to help account for the complexity of lignin. Reaction conditions and catalyst selection should consider the optimization of conversion of the most common motifs in lignin, including oligomers containing guaiacyl, syingyl, and phenyl groups.

At longer milling times, it was observed that the conversion of diphenyl ether was slightly higher than the collected yield of products. This could possibly be explained by the chosen condenser system not efficiently capturing all of the effluent product. A more robust condenser system, including a colder bath temperature at the outlet of the reactor, may recover additional products that were possibly lost in the current work. The detection of any missing products will help close the carbon balance differential at longer milling times. After the condenser has been improved to efficiently capture all products in the

effluent stream, the setup may be modified further to increase the temperature of the reactor. This should increase the rates of the hydrogenation reactions, and potentially allow for hydrodeoxygenation reactions to occur. Additionally, raising the temperature of the reactor will allow more products to leave with the effluent gas flow, creating a system where all of the products of the reaction are carried out of the reactor into the condenser. This may become important when using lignin as a feedstock or model compounds with higher degrees of functionalization than diphenyl ether. Reaction products like dicyclohexanol or methoxycyclohexanol which are less volatile than cyclohexanol might require a slightly elevated temperature to be efficiently carried out of the reactor by the effluent gas flow. This type of system would be more attractive to an industrial process instead of having to separate products from unreacted material in a post-reaction step.

Further work will also focus on applying this technology directly to lignin samples, rather than model compounds. It is possible that this reactor will provide an environment in which depolymerization and hydrogenation reactions can be performed simultaneously by combining lignin, a solid base, a supported metal catalyst, and a hydrogen stream. Products of this reaction will also eventually become volatile as they are converted to hydrogenated monomers and be carried to the condenser, effectively separating products from larger oligomers. These reactions may be supplemented by the addition of water or other reactants through the use of a bubbler placed prior to the inlet of the reactor. The addition of more water to the reactor will help determine if the reaction mechanism does involve a hydrolysis step, and also whether the reaction in the current work was limited by the amount of water in the system. Adding the water gradually through the use of a bubbler

may also alleviate plasticization effects caused by adding a large amount of water before beginning the reaction.

Finally, future work with this reactor system should not be limited to hydrogenation reactions. The feed gas may be switched to any other reactive gas, such as oxygen, as lignin has also been shown to depolymerize under oxidative conditions.[5, 8] Additionally, the reactions performed with the setup do not need to be limited to lignin valorization. A variety of organic and inorganic chemical reactions have been shown to be possible under mechanocatalytic conditions.[14] The scope of possible mechanocatalytic reactions can be greatly increased with the ability to perform reactions under atmospheres other than air.

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